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RECOMMENDED METHODS OF REDUCTION, NEUTRALIZATION, RECOVERY, OR DISPOSAL OF HAZARDOUS WASTE

VOLUME XIV: SUMMARY OF WASTE ORIGINS, FORMS, AND QUANTITIES

TRW Systems Group

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Volume XIV. Summary of Waste Origins, Forms, and Quantities

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in:

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

Under Section 212 of Public Law 91-512, the Resource Recovery Act of 1970, the U.S. Environmental Protection Agency is charged with preparing a comprehensive report and plan for the creation of a system of National Disposal Sites for the storage and disposal of hazardous wastes. The overall program is being directed jointly by the Solid and Hazardous Waste Research Laboratory, Office of Research and Development, National Environmental Research Center, Cincinnati, and the Office of Solid Waste Management Programs, Office of Hazardous Materials Control. Section 212 mandates, in part, that recommended methods of reduction, neutralization, recovery, or disposal of the materials be determined. This determination effort has been completed and prepared into this 16-volume study. The 16 volumes consist of profile reports summarizing the definition of adequate waste management and evaluation of waste management practices for over 500 hazardous materials. In addition to summarizing the definition and evaluation efforts, these reports also serve to designate a material as a candidate for a National Disposal Site, if the material meets criteria based on quantity, degree of hazard, and difficulty of disposal. Those materials which are hazardous but not designated as candidates for National Disposal Sites, are then designated as candidates for the industrial or municipal disposal sites.

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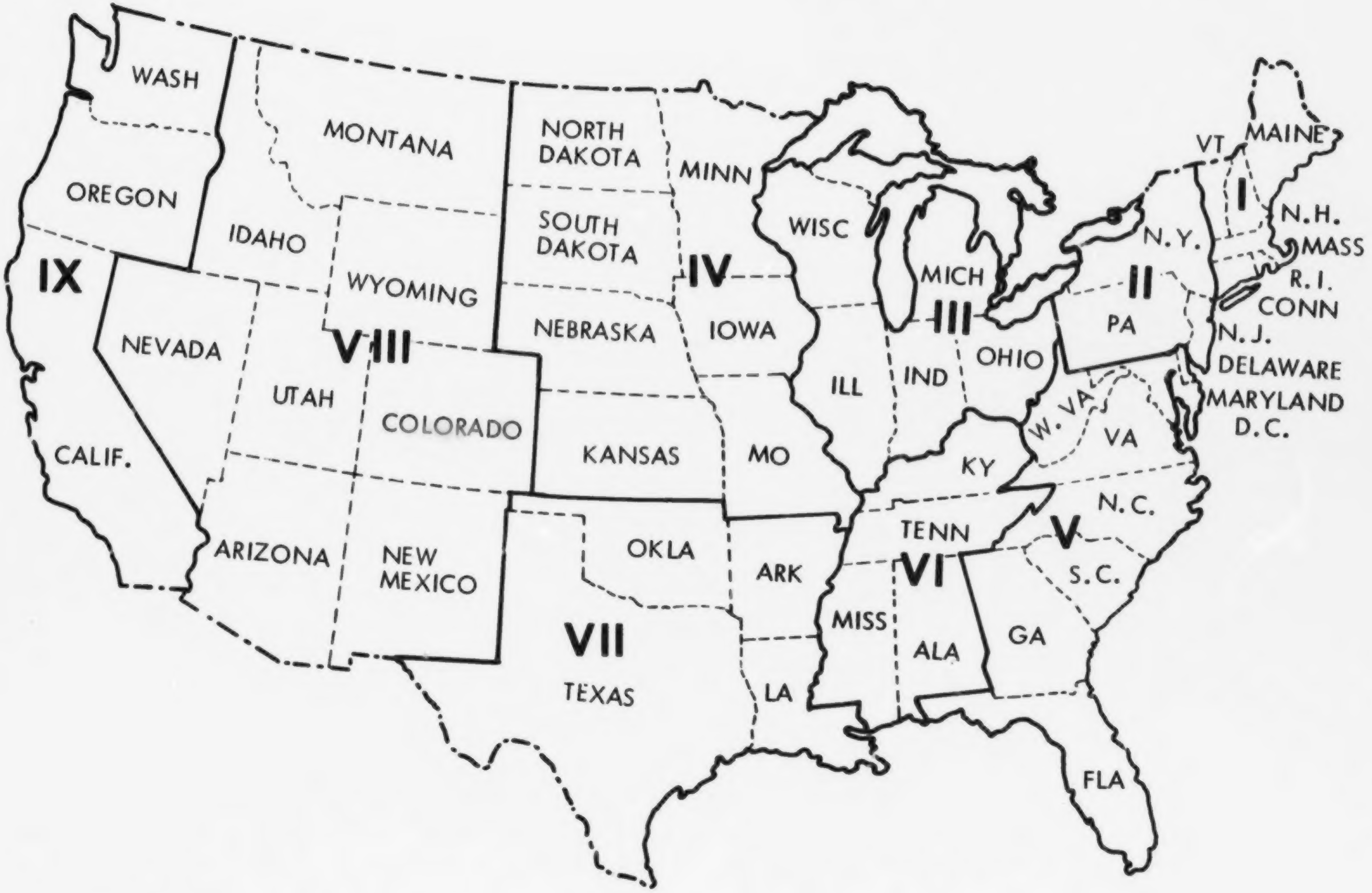
INTRODUCTION

This volume summarizes the TRW effort in the determination of the origins, forms, and quantities of hazardous wastes. The volume contains 16 separate reports.

The waste streams from some of the industries, such as the waste sludges from paint manufacture, were found to contain several hazardous waste stream constituents. To provide a complete treatment, and to avoid duplications in discussion, the first three reports in this volume describe the waste forms and quantity information according to the waste generation source. Wastes from paint manufacture and paint residue left in used paint containers are discussed in the report "Toxic Paint Wastes". Likewise, the manufacturing wastes from the electroplating and the battery industries are discussed separately in the reports "Cadmium, Copper, Cyanide, and Chromium Wastes from the Electroplating Industry" and "Cadmium, Lead, and Mercury Wastes from the Manufacture of Batteries". In the report on copper wastes, for example, detailed discussions of the copper wastes from electroplating are specifically referenced to the separate report on electroplating wastes.

The other 13 reports in this volume provide waste forms and quantity information for each group of hazardous waste stream constituents under investigation (such as the report "Wastes of Lead Compounds"). Each of these 13 reports consists of: (1) a short introductory section on the principal sources of the hazardous wastes; (2) a table (or tables) summarizing the total waste quantity information from each waste source and the geographical distribution of these wastes; (3) wherever applicable, a summary table (or tables) describing the forms and composition of the typical waste streams; and (4) for each major waste stream or waste source identified, an individual section discussing the data bases and the methods of estimation utilized in deriving the waste forms and quantity information, as well as the results of the findings.

The geographical distributions of the hazardous wastes are generally presented in terms of the standard U.S. Regions as identified by the Bureau of Census (Figure 1). The exceptions are the pesticide waste distributions, which are presented in terms of USDA Regions (described in the report "Pesticide Wastes"), and explosive wastes which are presented by state.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NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
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Figure 1. U.S. Bureau of Census Regions

TOXIC PAINT WASTES

Waste Sludges Containing Toxic Ingredients from Paint Manufacture

A paint is generally defined as a liquid vehicle containing a suspended pigment which is converted to an opaque solid film after application as a thin layer. The liquid vehicle consists basically of two components: (1) a binder, which forms the film and is composed of natural resins, synthetic polymers, or drying oils; and (2) a solvent, which is either water or an organic solvent. Other ingredients present in the paint may include driers to accelerate the drying of the film, plasticizers to give elasticity to the film, fungicides to inhibit the growth of mildews, and various other additives such as pigment-dispersing agents, antiskinning agents, defoamers, freeze-thaw stabilizers, etc.

Pigments are used in paint formulations to obscure the substrate, to impart color for aesthetic purposes, and to improve durability of the film. Millions of pounds of inorganic oxides, sulfates, and carbonates are consumed by the paint industry annually for the use of pigmentation (Table 1). In addition, materials such as talcs, clays, and chalks are used to aid processing and to maintain formulation stability. These materials are called extenders, fillers, or supplemental pigments. The inorganic pigments containing lead, cadmium, selenium, chromium (chromates and chromium oxide), and cyanides (Table 2) are mainly responsible for the toxicity of paints and the waste sludges from paint manufacture. With the exception of chrome oxide green, however, all the other pigments containing these toxic ingredients are normally only used for solvent-type paints. Both the chromate based pigments and the iron blues cannot be used in emulsions or water-based paints because they are unstable under the conditions of contact with aqueous solutions and alkalinity.

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TABLE 1

PIGMENTS CONSUMED BY THE COATINGS INDUSTRY - 1970[2495]

Pigments and Extenders	millions of lbs.
White pigments:	
Titanium dioxide	800
Zinc Oxide - lead free	50
Zinc oxide - leaded	10
White lead	10
Other	5
Total	875
Colored and black pigments:	
Carbon blacks	15
Red lead	20
Chrome green	5.4
Chrome oxide green	10.4
Chrome yellow and orange	63.5
Molybdate chrome orange	21.7
Zinc yellow	15.6
Iron blue	10.0
Cadmium red, yellow, and orange*	0.7
Other inorganic colors	116
Organic colors	12
Metallics (aluminum pastes, etc.)	20
Zinc dust	50
Total	367
Extenders:	
Calcium carbonate	350
Magnesium silicate (talc)	330
Clay	280
Barium sulfate (barytes)	100
Mica	60
Others	200
Total	1,320
Total pigments and extenders	2,562

*The estimates are based on the assumption that 25 percent of the cadmium pigments produced is consumed by the paint industry. Comsumption figure of 0.7 million lb is as the cadmium metal. About 51,000 lb of selenium are used in the cadmium pigments.

TABLE 2
PIGMENTS CONTAINING TOXIC INGREDIENTS

Pigment	Principal Chemical Component	Toxic Ingredient
White lead	$2PbCO_3 \cdot Pb(OH)_2$	lead
Leaded zinc oxide	$2PbSO_4 \cdot PbO + ZnO$	lead
Red lead	Pb_3O_4	lead
Cadmium yellow	CdS	cadmium
Cadmium orange	$CdS + CdSe$	cadmium, selenium
Cadmium red	$CdS + CdSe$	cadmium, selenium
Chrome yellow	$PbCrO_4$	lead, chromate
Chrome orange	$PbO \cdot PbCrO_4 + PbCrO_4$	lead, chromate
Zinc yellow	$4ZnO \cdot K_2O \cdot 4CrO_3 \cdot 3H_2O$	chromate
Molybdate orange	$PbCrO_4 + PbMoO_4$	lead, chromate
Chrome green	$PbCrO_4 + Fe(NH_4)Fe(CN)_6$	lead, chromate, cyanide
Chrome oxide green	Cr_2O_3	chromium oxide
Iron blue	$Fe(NH_4)\ Fe(CN)_6$	cyanide

Solvent- and water-based paint films are formed differently and employ different materials as binders. Solvent-based paint forms a film through a combination of organic solvent[*] evaporation and the catalytic polymerization of the drying oil. Binders or film forming materials used for solvent-based paints contain natural and synthetic resins, drying oils and fatty acids. Resins used in solvent-based paints include alkyds, epoxies, rosin-esters, urea-melamines, and to a lesser extent acrylics, phenolics, urethanes, hydrocarbons, vinyl-acetate and vinyl-chloride copolymers, and vinyl formal and butyral acetal resins (Table 4). Drying oils and fatty acids used in solvent-based paints include linseed oil and its fatty acid, soybean oil and its fatty acid, tall oil, tung oil, castor oil, safflower oil and oiticica oil (Table 5). Water-based paints, on the other hand, form a continuous film through evaporation of their water content and subsequent coalescence of the synthetic polymer particles. The formulation of the water-based paint consists basically of combining pigments and synthetic resin dispersions or latexes. The four major types of latexes used are polymers based on esters of acrylic acid, polyvinyl acetate, polyvinyl chloride, and styrene-butadiene.

In addition to the toxic inorganic pigments, phenyl mercury compounds have been added to paints for use as a mildewcide and to extend the shelf life of paints and constitute another major hazard associated with paints and waste sludges from paint manufacture.[†] Phenyl mercuric acetate, phenyl mercuric oleate, and di (phenyl mercuric) dodecenyl succinate represent the three types most commonly employed as paint additives. These phenyl mercury compounds are currently used almost exclusively for water-based paints in low concentrations of 0.004 to 0.1 percent (as mercury), with 0.01 to 0.05 percent being the average.[2576,2577] Mercury comsumption by the paint industry amounted to 654,000 lb in 1971.

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[*] Organic solvents used include aliphatic and aromatic hydrocarbons, ketones, esters, alcohols and glycols (Table 3).

[†] It is believed that mercury is no longer used in antifouling paints.

TABLE 3

SOLVENTS CONSUMED BY THE COATINGS INDUSTRY - 1970[2495]

Solvents	millions of lbs.
Hydrocarbons:	
Aliphatic	600
Aromatic	690
Total	1,290
Oxygenated:	
Ketones	815
Esters	250
Alcohols	555
Glycols	50
Glycol esters	10
Glycol ethers	95
Glycol ether-esters	80
Total	1,855
Other:	
Chlorinated products	10
Miscellaneous (terpenes, etc.)	30
Total	40
Total solvents	3,185

TABLE 4

RESINS CONSUMED BY THE COATINGS INDUSTRY - 1970[2495]

Resins	millions of lbs. (dry basis)
Resin:	
Synthetics	
Alkyds	600
Acrylics	220
Vinyls (PVac, PVC, etc.)	210
Cellulosics	75
Epoxies	68
Rosin esters	70
Urea-melamines	60
Phenolics	33
Styrenes	37
Urethanes	45
Hydrocarbons	30
Polyesters	7
Others	50
Total	1,505
Natural:	
Shellac	20
Rosin and others	30
Total	50
Total resin	1,555

TABLE 5

DRYING OILS AND FATTY ACIDS CONSUMED BY THE COATINGS INDUSTRY - 1970[2495]

	Drying Oils and Fatty Acids millions of lbs.
Oils:	
Linseed oil	192
Soybean oil	85
Tall oil	43
Tung oil	20
Castor oil	21
Fish/marine oil	7
Safflower oil	10
Coconut oil	5
Oiticica oil	4
Other oils	3
Total	390*
Fatty acids	65
Total	455

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*Excludes oils in coating resins.

The various operations in paint manufacture are wholly physical. The weighing, assembling, and mixing of the pigments and vehicles are normally done on the top floor of a paint plant. The batch masses are conveyed to the floor below, where grinding and further mixing take place. The paint is then transferred to the next lower floor, where it is thinned and tinted in agitated tanks, before being strained into a transfer tank or directly into the hopper of the filling machine on the floor below. Centrifuges, screens, or pressure filters are used to remove nondispersed pigments. The paint is poured into cans or drums, labeled, packed and moved to storage, each of these last few steps being completely automatic.

Solid wastes are generated from the manufacture of paints and allied products as a result of kettle washings and equipment clean-up. In the latex washing system, the waste water is first sent to a settling tank, where alum is added to facilitate flocculation. The waste water is then decanted, and drained into the sewers after any necessary pH adjustment. Sludge from the latex washing system are mainly disposed of in sanitary landfills,[2575] in spite of the fact that the toxic constituents in paint are not biodegradable and the leaching of these pollutants by percolating water could lead to gross ground and surface water contamination. Industry sources indicated that 1 gal. of sludge is produced for every 170 gal. of water-based paint product, and that the water-based paint sludge has the following general composition:[2576]

2.5 percent inorganic pigment (excluding titanium dioxide)
4.5 percent titanium dioxide
8.0 percent extenders
20.0 percent binders
65.0 percent water

The mercury concentration in the water-based paint sludge ranges from 0 to 700 ppm, the estimated average being 100 to 150 ppm.*

In the solvent washing system, the waste stream is normally pumped over to a storage tank and decanted. The solvent is recovered by distillation. The sludge obtained from the decantation step typically contains 20 percent inorganic pigment and extenders, 20 percent binders, and 60 percent organic solvents, with a heating value of 14,000 to 18,000 Btu/lb.[2576] The residue sludge from the solvent stills, however, has a higher solids content, and typically contains 35 percent inorganic pigment and extenders, 30 percent binders, and 35 percent organic solvents, with a heating value of 10,000 to 15,000 Btu/lb.[2576] Industry sources indicated that a total of 1 gal. of sludge is obtained from the decantation and solvent recovery operations for every 120 gal. of solvent-based paint product.[2575,2576,2578] The combined solvent-based paint sludge is characterized by the following composition:[2576]

---

*Based on confidential data from a state-wide survey conducted by the California State Water Resources Control Board.

4.5	percent inorganic pigment (excluding titantium dioxide)
8.5	percent titanium dioxide
14.5	percent extenders
25.0	percent binders
47.5	percent solvent

The solvent-based paint sludges are currently disposed of in sanitary landfills. As indicated previously, this is not a satisfactory procedure and incineration systems to handle solvent-based paint sludges are now under development.[2576] The solvent recovered from the still is used for cleaning purposes only, and contains 70 percent aliphatic hydrocarbons and 30 percent aromatic hydrocarbons.

Based on the waste generation factor of 1 gal. of sludge for every 120 gal. of solvent-based paint product, the quantity of pigments consumed by the coatings industry (Table 1), and a U.S. solvent-based paint production of 442 million gal. in 1971, it was estimated that 637,000 lb of lead, 137,000 lb of chromium (mostly in the form of chromates), 5,100 lb of cadmium, 370 lb of selenium, and 44,900 lb of cyanides are lost through 36,800,000 lb of solvent-based paint sludges per year (Table 6). In water-based paints, chrome oxide green and the phenyl mercury compounds are normally the only toxic ingredients of concern found in the paint product and the waste paint sludges. Again, based on the waste generation factor of 1 gal. of sludge for every 170 gal. of water-based paint product, the quantity of chrome oxide green and mercury consumed by the coatings industry, and a U.S. water-based paint production of 442 million gal. in

TABLE 6

WASTE SLUDGES CONTAINING TOXIC INDGREDIENTS FROM PAINT MANUFACTURE

Material	Bureau of Census Regions I	II	III	IV	V	VI	VII	VIII	IX	Total
	Annual Waste Production (lb/yr)									
Solvent-Based Paint Sludge										
Lead	16,000	140,000	196,000	42,000	55,000	30,000	47,000	8,000	103,000	637,000
Chromium	3,000	30,000	42,000	9,000	12,000	7,000	10,000	2,000	22,000	137,000
Cadmium	150	1,100	1,550	350	450	250	400	50	800	5,100
Selenium	10	80	115	25	30	15	25	5	60	370
Cyanides	1,100	9,900	13,800	2,900	3,800	2,150	3,350	550	7,300	44,900
Sludge	0.92×10^6	8.12×10^6	11.32×10^6	2.40×10^6	3.16×10^6	1.76×10^6	2.74×10^6	0.44×10^6	5.97×10^6	36.83×10^6
Water-Based Paint Sludge										
Chromium	240	2,160	3,010	640	840	470	730	120	1,590	9,800
Mercury	45	395	555	120	155	85	135	20	290	1,800
Sludge	0.65×10^6	5.74×10^6	7.99×10^6	1.70×10^6	2.23×10^6	1.24×10^6	1.93×10^6	0.31×10^6	4.21×10^6	26.0×10^6

1971, it was estimated that 9,800 lb of chromium (as chromium oxide) and 1,800 lb of mercury are lost through 26,000,000 lb of water-based paint sludges per year (Table 6). The geographical distribution of these waste paint sludges was computed on the basis of the regional distribution of "value added by manufacture" dollar amounts for paints and allied products and by Bureau of Census regions (Table 6).

Old Paint

The paint residues left in containers discarded in municipal dumps often contain toxic ingredients and could lead to possible contamination of the soil and ground water. The composition of the old paint, after evaporation of the solvents, is approximately described by the pigment volume concentration (PVC) of the paint. The pigment volume concentration is defined simply as:

$$\text{PVC} = \frac{\text{volume of pigment in paint}}{\text{volume of pigment in paint + volume of nonvolatile vehicle constituents in paint}}$$

PVC is generally considered as the most important indicator in paint formulation, and controls such factors as gloss, reflectance rheological properties, washability, and durability. As a consequence, there is usually a range of PVC for a given paint, varying between 25 and 45 percent.

The amount of paint residues and their toxic constituents were computed with the assumptions that (1) 5 percent of the paint is unused and left in the containers; and (2) the nonvolatile portion accounts for 50 percent of the paint. It is estimated that 4,410,000 lb of lead, 963,000 lb of chromium (mostly as chromates); 35,300 lb of cadmium; 2,560 lb of selenium; 311,000 lb of cyanides; and 32,700 lb of mercury could be lost each year through the 221,000,000 lb of paint residue left in paint containers (Table 7). The geographical distribution of these paint residue wastes was calculated on the basis of the population distribution in the United States by Bureau of Census regions (Table 7).

As the old paints are normally discarded in their containers, the types and numbers of containers used by paint manufacturers are also of

TABLE 7
OLD PAINT

	Bureau of Census Regions									
Material	I	II	III	IV	V	VI	VII	VIII	IX	Total
	Annual Waste Production (lb/year)									
Lead	2.58×10^5	8.13×10^5	8.81×10^5	3.28×10^5	6.69×10^5	2.77×10^5	4.22×10^5	1.81×10^5	5.81×10^5	4.41×10^6
Chromium	0.56×10^5	1.78×10^5	1.92×10^5	0.72×10^5	1.46×10^5	0.61×10^5	0.92×10^5	0.40×10^5	1.27×10^5	9.63×10^5
Cadmium	2,100	6,500	7,000	2,600	5,400	2,200	3,400	1,400	4,700	35,300
Selenium	150	470	510	190	390	160	240	110	340	2,560
Cyanides	0.18×10^5	0.57×10^5	0.62×10^5	0.23×10^5	0.47×10^5	0.20×10^5	0.30×10^5	0.13×10^5	0.41×10^5	3.11×10^5
Mercury	1,900	6,000	6,500	2,400	5,000	2,100	3,100	1,400	4,300	32,700
Old Paint	13×10^6	41×10^6	44×10^6	16×10^6	34×10^6	14×10^6	21×10^6	9×10^6	29×10^6	221×10^6

some concern. Extrapolation of the data presented in the recent survey by the National Paint and Coatings Association indicates that the containers used are predominantly of the 1 quart and 1 gallon size metal type.[2498] For the year 1970, the quantities of each size container used are: 1 pint containers, 60 million; 1 quart containers, 160 million, 1 gallon containers, 320 million; 5 gallon containers, 16 million; and 55 gallon drums, 3.7 million.

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CADMIUM, COPPER, CYANIDE, AND CHROMIUM WASTES FROM THE ELECTROPLATING INDUSTRY

Electroplating and metal finishing waste streams can contribute directly to stream pollution resulting from the content of toxic and corrosive materials such as cyanide, acids, and metals.

Wastes from an electroplating plant may range from nontoxic to highly toxic and/or corrosive. Innocuous effluents are obtained only by the use of thorough in-plant waste treatment methods. Highly lethal or corrosive effluents are generally the result of the accidental or intentional discharge of concentrated solutions. The incidence of this type of discharge is minor in the metal finishing field. [0783]

The sources of the liquid, solid, and semi-solid wastes generated in the electroplating industry include the following:

(1) rinse waters from plating, cleaning, and other surface finishing operations;

(2) concentrated plating and finishing baths that are intentionally or accidentally discharged ;

(3) wastes from plant or equipment cleanup ;

(4) sludges, filter cakes, etc., produced by naturally occurring deposition in operating baths or by intentional precipitation in the purification of operating baths, chemical rinsing circuits, etc., when flushed down sewers ;

(5) regenerants from ion exchange units; and

(6) vent scrubber waters.

The most important of these wastes, especially from the standpoint of the smaller plater, is the rinse water.[0783] This is the constantly flowing, production oriented stream which is generally so large in volume that some form of concentration is warranted before it can be economically transported to a central disposal facility for treatment.

Some of the general methods used to treat or reduce the volume of rinse waters from electroplating shops include ion exchange, precipitation, chemical destruction, chemical reduction, biological destruction on trickling filters, evaporation, and adsorption with activated-carbon beds. These treatment methods are described in more detail in the Profile Reports on cadmium, copper, cyanide, and chromium compounds.

The wastes from the electroplating industry include liquid, slurry, sludge, and solid forms depending upon the degree of concentration. Rinse waters, for example, may be concentrated by passing through evaporators. Information on the forms and composition of some typical waste streams from electroplating that contain cadmium, copper, and cyanide compounds was provided by Rollins Environmental Services and is summarized here (Tables 1, 2, 3). The forms and composition of chromium containing waste streams from metal finishing are discussed separately in the report "Wastes of Chromium Compounds".

Cadmium Wastes

It is estimated that there are 1,440,000 lb of water soluble cadmium waste (as cadmium) generated per year by the electroplating industry. This number was computed by applying a 18 percent waste generation factor to the total amount of cadmium used in the electroplating industry each year. The waste generation factor was supplied by L. E. Lancy of Lancy Laboratories.[2287] The total waste quantity was based on cadmium consumption of approximately 8,000,000 lb per year by the electroplating industry

TABLE 1
TYPICAL ELECTROPLATING WASTES CONTAINING CADMIUM

Waste Description
1.5 % cadmium cyanide and 8.5 % sodium cyanide in a 3 % caustic solution, with trace of other metals.
Solid waste containing 3 % cadmium oxide and 16 % cadmium metals with alkali carbonates--hangers from plating bath.
300 to 500 ppm cadmium chromate with aluminum alkaline salts, organic cleaners, and 95 % water--wash water.
Liquid slurry containing 5 % cadmium cyanide and 5 % sodium cyanide in 10 % aqueous sodium hydroxide.

TABLE 2

TYPICAL ELECTROPLATING WASTES CONTAINING COPPER

Waste Description
2 % copper cyanide, 6 % sodium cyanide, sodium sulfonate, hydrocarbons, and zinc phosphate in 83 % water.
Alkaline cyanide solutions having copper concentrations of 50 to 10,000 ppm, alkaline concentrations of 1 to 20 % as sodium hydroxide, and chromium nickel, and lead.
Solid crystalline waste containing 15 % copper in a copper cyanide-sodium cyanide salt and traces of other metals.
2 % copper cyanide and 5 % sodium cyanide in a 10 % sodium hydroxide solution.
5 % copper in 17 % sulfuric acid.

TABLE 3

TYPICAL ELECTROPLATING WASTES CONTAINING CYANIDES

Waste Description
Liquid waste containing 15 % sodium cyanide, a 10 % mixture of sodium ferro and sodium ferricyanides, and traces of nickel and zinc.
Stripping solution containing 13 % sodium cyanide, sodium hydroxide, and 600 ppm copper.
0.8 % cyanide, 3,300 ppm zinc, 165 ppm nickel, and trace of silver in a 1 % sodium hydroxide solution.
Slurry containing 20 % sodium ferrocyanide, 2% zinc and insoluble material, and 50 % water.
Slurry containing 2.5 % zinc ferrocyanide, 2 % calcium fluoride, 3 % chromic hydroxide, and 80 % water.
1 % potassium ferrocyanide and less than 50 ppm lead, nickel, chromium, and copper combined in an aqueous 10 % sodium hydroxide solution.
3 to 5 % sodium cyanide and 1 to 3 % nickel, cadmium, copper, and zinc in an aqueous 10 % sodium hydroxide solution.

(this figure represents the amount of cadmium compounds used to make up the plating baths and the amount of cadmium metal used in the plating electrodes).[2286]

The geographical distribution of these wastes was computed on the basis of the distribution of "value added by manufacture" dollar amounts for finished metal products in the United States and by Bureau of Census regions (Table 4).

Copper Wastes

It is estimated that there are 2,106,000 lb of copper wastes (as copper) generated by the electroplating industry each year. This number was computed by using the same 18 percent waste generation factor that was used for cadmium electroplating. Industry sources indicated that the 18 percent figure is the representative copper waste factor within the electroplating industry.[2604] The total waste quantity was based on copper consumption of 11,700,000 lb per year by the electroplating industry (this figure includes the amount of copper compounds and copper metal electrodes used).[2603]

The geographical distribution of these wastes was computed on the basis of the distribution of "value added by manufacture" dollar amounts for finished metal products in the United States and by Bureau of Census regions (Table 4).

Cyanide Wastes

Cyanide compounds (cadmium cyanide, copper cyanide, etc.) are used extensively to make up the plating baths in the electroplating industry because cyanide compounds are good complexing agents. This complexing action increases the solubility of the metal cyanide salts and makes the electroplating operation more effective.

It is estimated that there are 21,320,000 lb of cyanide wastes (as cyanide) generated in the electroplating industry each year. This number

TABLE 4
ELECTROPLATING WASTES

Material	Bureau of Census Regions									
	I	II	III	IV	V	VI	VII	VIII	IX	Total
	Annual Waste Production (lb/year)									
Cadmium	1.88×10^5	4.10×10^5	4.64×10^5	0.65×10^5	0.70×10^5	0.33×10^5	0.52×10^5	0.10×10^5	1.48×10^5	14.40xx 10^5
Copper	2.75×10^5	5.99×10^5	6.78×10^5	0.95×10^5	1.03×10^5	0.48×10^5	0.76×10^5	0.15×10^5	2.17×10^5	21.06×10^5
Cyanide	2.78×10^6	6.07×10^6	6.86×10^6	0.96×10^6	1.04×10^6	0.49×10^6	0.77×10^6	0.15×10^6	2.20×10^6	21.32×10^6

was estimated from information presented in a report by the Battelle Memorial Institute.[2224] The mean cyanide waste load per plant (8,170 lb per year) was calculated from a graph in this report that was prepared using data collected from 162 plating shops in the United States.[2224] This mean waste load was then multiplied by the number of plants in the United States that use cyanides in their electroplating operation (approximately 2,600 plants*)[2602] to obtain the total waste quantity.

The geographical distribution of these wastes was computed on the basis of the distribution of "value added by manufacture" dollar amounts for finished metal products in the United States and by the Bureau of Census Regions (Table 4).

Chromium Wastes

Chromium compounds are formulated for use as cleaning agents, oxidizing agents and surface preparation agents as well as the chemicals used to electroplate the decorative chrome surface. The wastes are generated from the washing of the metal parts as well as spills, tank leakage, etc. Many of the metal treatment tanks become exhausted and have to be periodically drained and this is a major portion of the waste load.

It is very difficult to distinguish between the amount of chromium wastes generated in electroplating and the amount generated in the other metal finishing processes. More detailed information on the quantities of chromium wastes and forms and composition of the waste streams can be found in the report "Wastes of Chromium Compounds".

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*Eighty-seven percent of the plating shops in the United States use cyanides in their operation.[2602]

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2603. Personal communication. Bob Trees, Metal Finishing Suppliers Assoc. to D. Dal Porto, TRW Systems. Dec. 7, 1972. Amount of copper used in electroplating annually.

2604. Personal communication. Jim Zievers, Industrial Filter Corporation to D. Dal Porto, TRW Systems. Dec. 7, 1972. Copper wastes from electroplating.

CADMIUM, LEAD, AND MERCURY WASTES FROM THE MANUFACTURE OF BATTERIES

Nickel-Cadmium Batteries

There are two distinct types of nickel-cadmium cells--the pocket plate (Jungner type) cell and the sintered-plate cell.

The positive and negative plates of the Junger cell are usually similar in construction, consisting of perforated pockets which contain the active materials. The pockets for both positive and negative plates are made from perforated steel ribbon which has been nickel-plated and annealed in hydrogen. Pockets of the negative plates are filled initially with cadmium oxide or cadmium hydroxide, either of which is reduced to metallic cadmium on the first charge. Most manufacturers of these cells add iron (5 to 30 percent) to the cadmium in order to obtain the required degree of fineness of the cadmium.[2616]

The pockets for holding the active material of both positive and negative plates of Nicad batteries are standardized at half an inch, but the length may be varied. These are pressed into grids, usually called frames, made of nickel-plated steel. The plates are assembled into elements with rods of polystyrene being used as separators between plates of opposite polarity. Sheet hard-rubber separators are used between the sides of the element and the inside of the steel container of the cell. The container is welded along all seams and at the top and bottom. Terminal posts are sealed through rubber glands.[2616]

Industry sources indicate that the production of pocket-plate type batteries does not generate much cadmium waste. This is because the active chemicals used are solids and not solutions or pastes. When good housekeeping methods are used within the plant, there is almost no waste generated.[2609]

The manufacture of sintered-plate batteries, however, does generate some waste. This type of cadmium battery differs materially in construction and performance from the pocket-plate battery described above.

The plates consist of a highly porous structure of nickel impregnated with the active materials nickel oxide and cadmium. The plates are called plaques before being impregnated with the active materials. To obtain plaques of 60 to 90 percent porosity, it is necessary to use a nickel powder of low apparent density. The powder sinters in a protective atmosphere without the need for compacting at temperatures as low as 500 C, but higher temperatures are generally used.

Grids are usually a coarsely woven wire cloth of about 20 mesh and may have a frame around the wire. A thin nickel strip is welded to the cloth to provide the lug. The grids are usually of nickel, but nickel-plated iron has been used.

The plaques are cut (in the form of the plate) from a block of graphite about 1 in. thick. The carbonyl nickel is sifted into the opening to about half depth, and then the grid is laid on it and covered with the other half of the powder. A graphite cover closes the mold. The sintering furnace is provided with a cooling chamber into which the graphite block passes after 10 minutes' heating. In the protective atmosphere of nitrogen and dissociated ammonia the plaque is finished, and it then has about 80 percent porosity.

Impregnation is accomplished in solutions of nickel and cadmium salts. Electrolysis is done in an electrolyte of 25 percent sodium or potassium hydroxide heated to nearly 100 C. The current density is high and maintained for about 20 minutes while vigorous gassing occurs. The washing that follows is done with deionized water (the components of tap water are detrimental to the lifetime performance of the battery) and may last 3 hours until the effluent water has a pH of 9. The plates are dried at 80 C.[2609] This cycle of impregnation is repeated 4 or 5 times, each succeeding cycle making the washing more difficult. The finished plates are assembled into cells, using plastic rods as separators.

A typical impregnation bath may be composed of 8 percent cadmium oxide, 0.6 percent nicklic oxide, 14 percent potassium hydroxide, and trace metals.

Industry contacts indicate that the major source of waste in the manufacture of sintered-plate batteries is the wash water that is used to remove excess material from the plates.[2609] A typical wastewater effluent may contain cadmium hydroxide, potassium hydroxide (as high as 1000 ppm), and potassium nitrate. The concentrations are fairly high because the deionized water commonly used is expensive and minimal quantities are applied.[2609]

It is estimated that there are 3,700 lb of cadmium waste (as cadmium) generated in the production of sintered plate nickel-cadmium batteries annnually by the seven U.S. manufacturers (Table 1). This estimate is based on a waste generation factor of 4 lb of cadmium waste (as cadmium) produced for every 3,000 gal. of wash water effluent.[2609] The waste factor was applied to a combined wash water effluent of approximately 2.8 million gal. per year for the seven U.S. manufacturers. The largest battery manufacturer has an effluent of 1 million gal. per year and the other 6 manufacturers have a combined effluent of 1.8 million gal. per year. All of the above data was supplied by A. D. Little, Inc.[2609]

The geographical distribution of these wastes was determined on the basis of the plant locations of the Nicad battery manufacturers and by Bureau of Census Regions (Table 2).

Lead-Acid Batteries

The battery industry is the largest consumer of lead in the United States--about 500,000 tons were used in 1968. Eighty percent of this is returnable, however, as secondary metal when the batteries are discarded.[2616]

There are basically two types of lead-acid batteries--pasted plates and Planté plates. The essential difference between the two is that the active materials of Planté plates are derived from the body of the plate

TABLE 1

NICKEL-CADMIUM BATTERIES

Firm	Location
Alkaline Batteries Corporation	Easthampton, Massachusetts
Eagle Picher Industries, Incorporated Precision Products Department	Colorado Springs, Colorado
General Electric Company Battery Business Division	Gainsville, Florida
Goulton Industries, Incorporated	Metuchen, New Jersey
Marathon Battery Company	Cold Spring, New York
Nicad Division, Gould Incorporated	St. Paul, Minnesota
NIFE Incorporated	Copiagne, New York

TABLE 2
WASTES FROM BATTERY MANUFACTURE

Material	Bureau of Census Regions									
	I	II	III	IV	V	VI	VII	VIII	IX	Total
	Annual Waste Production (lb/year)									
Cadmium	530	1,600	-	530	530	-	-	530	-	3,720
Lead	2.56×10^5	4.70×10^5	2.29×10^5	0.46×10^5	0.70×10^5	0.08×10^5	0.25×10^5	0.15×10^5	2.21×10^5	13.40×10^5

itself, whereas for pasted plates they are formed from oxides or other pastes applied to the plate mechanically. The manufacture of pasted plate batteries contributes the major portion of the lead wastes generated from battery manufacturing. For this reason, the following discussion is limited to pasted plate batteries.

The grids of lead acid batteries serve as supports for the active material of the plates and conduct the electric current. They also have an important function in maintaining a uniform current distribution throughout the mass of the active material. The grids are cast, for the most part, of an alloy of lead and antimony.

The pastes now commonly used in making the pasted-plate batteries are prepared by mixing some particular lead oxide or a blend of oxides with a dilute solution of sulfuric acid. Reactions occur that result in the formation of basic lead sulfate and the liberation of considerable heat. The lead sulfate is the cementing material which makes a firm plate that can be handled in the processes to follow. The lead sulfate also expands the paste and this has an important effect on the subsequent operating characteristics of the finished battery. Too little expansion results in hard, dense plates and needless limitation of the ampere-hour capacity of the battery. They may fail in service by buckling. On the other hand, too great expansion may result in shedding of the active material and thereby shorten the useful life of the battery.[2616]

The paste is applied to the grids by hand labor in many of the smaller manufacturing plants and by machine pasting equipment in most of the larger plants. When the work is done by hand, the paste is spread upon the grids with a wooden spatula or a smoothing trowel. Sufficient pressure must be applied to force the paste into intimate contact with the cross bars of the grid. The grids must be free from grease and dirt before pasting is begun. Sometimes they are washed and dipped in a dilute solution of sulfuric acid before being pasted.

Machines of several types have been developed for pasting the plates. In the machine operation, the grids pass under a hopper from which approximately the right amount of paste is received. This is pressed into the grids as they pass along, and the excess paste is removed. Sometimes the plates are partially dried before leaving the machine.[2616]

The lead wastes from the battery industry are generated largely in the mixing of the pastes and the application of the pastes to the grids. A typical waste sludge may contain 2,500 ppm of lead sulfate, a trace of copper hydroxide, and neutralized sulfuric acid.*

It is estimated that there are 1,340,000 lb of lead waste (as lead) generated in the manufacture of lead-acid batteries each year. This number was computed by employing the same waste generation factor (0.67 percent of the material input is wasted) as for the manufacture of cadmium-nickel cells and assuming that of the total amount of lead used each year in the battery industry, 20 percent of it is used to make the lead-acid battery paste.

The geographical distribution of these wastes was determined on the basis of the distribution of "value added by manufacture" dollar amounts for electrical supplies produced in the United States and by Bureau of Census regions (Table 2).

Mercury Cell Batteries

Confidential industry sources indicated that mercury wastes from battery manufacturing are insignificant. The only mercury waste stream generated in the production of mercury cell batteries comes from the wash water used to clean mechanical equipment in the assembly line. This is a very low volume waste stream. The methods for treating this waste stream are: (1) addition of sodium sulfide to precipitate out mercuric sulfide;

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*Rollins Environmental Services data.

and (2) reduction to elemental mercury with sodium borohydride or zinc. The mercury or mercuric sulfide is then collected by filtration and reclaimed for its mercury value.

The larger battery manufacturers also make their own mercury chemicals (mercuric oxide) to be used in the production of their mercury cell batteries. In this case, there is an aqueous waste stream which may contain 0.1 to 0.5 percent mercury (mostly mercuric oxide with some mercuric chloride), and sodium chloride. This waste stream is usually combined with the waste stream from the battery production line and the treatment methods described above are employed.

The same confidential sources from the battery manufacturing industry also indicated that 10 to 20 percent of the mercury cells produced are currently being recycled to the battery manufacturers for the reclamation of the mercury value. This would imply that 80 to 90 percent of the mercury contained in the batteries eventually end up in landfills, dumps and incinerators and find their way into the environment.*

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*The quantity of mercury used in batteries each year is not available. Total mercury consumption for the general category "electrical apparatus" amounts to 1.29 million lb in 1971.

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PESTICIDE WASTES

The disposal of surplus pesticides and pesticide contaminated wastes is a problem of growing concern in recent years. Pesticide wastes that warrant transportation to National Disposal Sites for treatment come from three major sources:

(1) manufacturing wastes from pesticide producers and formulators;

(2) empty pesticide containers with pesticide residues from professional applicators and agricultural users;

(3) surplus pesticides stored in government facilities.

Manufacturing Wastes

Pesticide manufacturers produce a variety of pesticide wastes. Although aqueous waste streams and gas streams containing pesticides and related toxicants are usually treated at the production site, there are other solid, semi-solid, and liquid pesticide contaminated wastes currently disposed of largely in landfill sites without adequate prior detoxification.* Virtually every pesticide manufacturer produces contaminated solvents and process solutions containing unreacted ingredients, unrecovered products and undesired by-products and in spite of the extensive efforts made to minimize these process losses, the wastes are generated because a point is usually reached where further recovery and recycle of the waste streams and their constituents are no longer economically or technically feasible. Pesticide ingredients may often be found to be concentrated in still bottoms or filter media. In addition, normal plant trash such as bags, rags, empty containers also often contain an unknown amount of pesticide residue.

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* Several major pesticide manufacturers have incineration facilities to dispose of these types of wastes.

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Formulating plants receive pesticide concentrates from manufacturers. Pesticide formulation processes are primarily batch mixing operations where the appropriate active ingredients, solvents, or carriers, and the necessary additives such as emusifying agents are blended together in ratios needed to give the desired product. Frequently, the same equipment is used to produce a number of pesticide formulations containing different active ingredients and solvents and great care must be taken to prevent cross-contamination during the formulation process. Cleaning of liquid formulation process equipment generally involves one to five rinses with 20 to 50 gal. of the solvent used in the previous formulation.[2501] In most cases, the solvents used for rinsing are collected in sumps or evaporative basins along with liquid wastes from occasional washdown of other plant facilities. Evaporative basins of this type could be used for several years in some parts of the country before concentrated liquid wastes and the accumulated sludges have to be removed by contract disposal services. Dry formulation plants, on the other hand, generally clean their equipment by flushing with a dry inert material before producing a different product and it is often possible to save the flushing material for use in later production.[2501]

Information on the representative forms of pesticide manufacturing wastes was provided by Rollins Environmental Services (Table 1). To summarize, the principal types of wastes from pesticide manufacturers and formulators are: (1) solid wastes containing 0.1 to 10 percent active ingredients on rags, bags, paper, fiber drums, steel drums, filter solids, etc.; (2) still bottoms containing active ingredients which are usually produced only in small quantities; (3) solvent cleanup wastes containing 1 to 10 percent active ingredients and inert carriers in aqueous or organic solutions which are mainly produced by pesticide formulators: (4) spill cleanup and floor washing wastes containing 1 to 10 percent active ingredients in aqueous solution or organic solvent which are usually produced in very small quantities; (5) process wash water containing a few ppm to 0.1 percent active ingredients in aqueous solution; (6) process solutions that may contain up to 50 percent active ingredients, decomposition products, undesired by-products etc.; and (7) off-spec material that can usually be reworked into the process.

TABLE 1

REPRESENTATIVE PESTICIDE MANUFACTURING WASTES

Solid Wastes:

- 2 to 5 % Methomyl on fiber drums
- 2 % Temik, 5 % Carbowax on solid matrix
- 0.1 to 10 % Methyl Parathion in plant trash
- --contaminated paper, gloves, sample bottles, etc.

Semi-Solid and Liquid Wastes:

- 2.5 % Heptachlor and related compounds; 10 % diatomoceous earth in aqueous slurry--solvent cleanup
- 10 % mixed Malathion and Parathion; 5 to 7 % mixed intermediates; 3 to 4 % Carbaryls; 5 to 10 % diatomoceous earth; 3 to 5 % organic solvent in aqueous slurries--solvent cleanup
- 11 to 40 % mixed phosphorothioates; 10 to 15 % phenates; 30 % alcohols; sodium sulfate inorganic phosphites, filter aid and 0 to 20 % water--still bottoms and solvent cleanup
- 1 to 5 % 2,4-D and/or 2,4,5-T in mixed solvents including toluene and xylene--solvent cleanup
- 5 to 10 % Atrazine; 5 to 10 % other triazines and by-products; 85 % toluene--solvent cleanup
- 1 to 2 % Randox; 23 % trichlorobenzye chloride; 65 % aromatic solvent--solvent cleanup
- 20 to 25 % 2,4-D; 20 to 25 percent 2,6-D; 10 to 15 % mono- and trichlorophenoxy acetic acids,solvents and water--plant shutdown residue
- 0.01 to 0.1 % methyl arsenate and other related compounds; 3 % soluble organics in alkaline solution--process wash water
- 10 % Dithane in water with cleaning agents--spills and floor washings
- 30 % DDT; 10 % trichloroethane and benzylchlorophenol; 60 % mixed hydrocarbons--process solution
- 10 % DDT; 11 to 18 % DDT decomposition products; 5 % benzensulfonic acid; 30 % aqueous sulfuric acid--process solution
- 45 % mixed methyl esters and thioesters of phosphoro dithioate compounds; 5 % mercaptans and hydrogen sulfide; 50 % organic solvent --process solution
- 7 % Torpedo (dichloroethyl-dinitrotoluidene) in aqueous 38 % nitric acid, 18 % phosphoric acid, 14 % hydrochloric acid--process solution

Among the pesticide manufacturing wastes described here, only the solid wastes, the contaminated solvents, and the process solutions are produced in large volumes. A major pesticide manufacturer has indicated that an average of 3 lb of pesticide active ingredient are lost through these wastes per 1,000 lb of pesticide active ingredient produced,[2290] and the pesticide production wastes by USDA Regions (Table 2) have been computed by using the information on the distribution of pesticide production plants (Table 3), the estimated U.S. herbicide, insecticide, and fungicide production figures (Tables 4, 5, 6), and the above production loss figure (Table 7). For the specific pesticides which have been profiled, the types and quantities of wastes generated in their manufacture have been obtained from literature and industry sources and by TRW estimates and are summarized in this report (Tables 8 and 9). In the absence of any actual data, rough estimates on pesticide manufacturing wastes could be made based on the following model:

(1) solid wastes --0.5 percent active ingredients on contaminated fiber material and 0.2 lb of waste per lb of pesticide active ingredient products;

(2) contaminated solvents--5 percent active ingredients in organic solvents and 0.02 lb of waste per lb of pesticide active ingredient formulated;

(3) process solution--10 percent active ingredients in organic solvent and 0.01 lb of waste per lb of pesticide active ingredient produced.

The solid waste generation factor of 0.2 lb of waste per lb of pesticide active ingredient produced is the average of the figures provided by the two sources where reliable and well-documented records of solid waste quantity information are available. The first source, a major organophosphorus manufacturer, indicated that approximately 0.34 lb of solid waste are generated per lb of pesticide active ingredient produced. The second source, a DDT manufacturer, provided a lower waste generation factor of 0.16 lb of solid waste per lb of pesticide active ingredient produced.[2501] The estimate of 0.5 percent pesticide active ingredients in the solid wastes was based on Rollins Environmental Services data.

TABLE 2
USDA REGIONS

Region 1, North-Eastern

- New Hampshire
- Maine
- Vermont
- New York
- New Jersey
- Pennsylvania
- Delaware
- Maryland
- Massachusetts
- Rhode Island
- Connecticut

Region 2, Appalachian

- Virginia
- West Virginia
- North Carolina
- Kentucky
- Tennessee

Region 3, South-Eastern

- South Carolina
- Georgia
- Florida
- Alabama

Region 4, Delta States

- Mississippi
- Arkansas
- Louisiana

Region 5, Corn Belt

- Ohio
- Indiana
- Illinois
- Iowa
- Missouri

Region 6, Lake States

- Michigan
- Wisconsin
- Minnesota

Region 7, Northern Plains

- North Dakota
- South Dakota
- Nebraska
- Kansas

Region 8, Southern Plains

- Oklahoma
- Texas

Region 9, Mountain States

- Montana
- Idaho
- Wyoming
- Colorado
- New Mexico
- Arizona
- Utah
- Nevada

Region 10, Pacific States

- Washington
- Oregon
- California
- Alaska*
- Hawaii*

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* Although Alaska and Hawaii are in Region 10, they were not included in the pesticide waste estimates which refer to USDA regions.

TABLE 3

PESTICIDE PRODUCTION PLANT LOCATIONS IN 1969[0449]

USDA Region & State	No. of Plant Sites
Region 1, North-Eastern	
New Hampshire	0
Maine	0
Vermont	0
New York	12
New Jersey	15
Pennsylvania	8
Delaware	0
Maryland	3
Massachusetts	7
Rhode Island	0
Connecticut	1
Region 2, Appalachina	
Virginia	5
West Virginia	1
North Carolina	16
Kentucky	1
Tennessee	3
Region 3, South-Eastern	
South Carolina	5
Georgia	18
Florida	18
Alabama	12
Region 4, Delta States	
Mississippi	9
Arkansas	5
Louisiana	7
Region 5, Corn Belt	
Ohio	10
Indiana	1
Illinois	15
Iowa	7
Missouri	9
Region 6, Lake States	
Michigan	7
Wisconsin	7
Minnesota	5
Region 7, Northern Plains	
North Dakota	0
South Dakota	0
Nebraska	4
Kansas	4
Region 8, Southern Plains	
Oklahoma	3
Texas	34
Region 9, Mountain States	
Montana	0
Idaho	1
Wyoming	0
Colorado	7
New Mexico	0
Arizona	11
Utah	0
Nevada	1
Region 10, Pacific States*	
Washington	8
Oregon	4
California	56

Total U.S. Plant Sites = 340

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* Although Alaska and Hawaii are in Region 10, they were not included in the pesticide waste estimates.

TABLE 4

ESTIMATED MAJOR U.S. HERBICIDE PRODUCTION IN 1971[2276,2277]

UNITS IN MILLION POUNDS

Benzoic	
Amiben	20
Banvel	2
Betasan	<1
Dacthal	2
Lasso	20
Naptalam	2
PCB and Salts	46
Picloram	3
Propanil	6
Ramrod	23
Silvex	3
2,3,6-TBA	2
Total	∼130

Triazine	
Amitrole	1
Aatrex	90
Princep	5
Propazine	4
Total	∼100

Phenyl-urea	
Chlorobenzilate	2
Chloroxuron	<1
Diuron	6
Monuron	<1
Siduron	<1
Linuron	2
Total	∼13

Phenoxy	
2,4-D	45
2,4,5T	6
Total	∼51

Dinitro	
Benefin	1
Dinoseb	3
Planavin	2
Trifluralin	25
Total	∼31

Chlorinated Aliphatic	
Dalapon	5
Randox	10
TCA	1
Total	16

Organic Arsenical	
Cacodylic Acid	2
DSMA-MSMA	35
Total	37

Carbamate	
Avadex	<1
Avadex BW	<1
Azak	<1
Barban	<1
Eptam	5
Ro-Neet	<1
Sutan	6
Tillam	1
Vegadex	<1
Vernam	2
Total	∼20

Other Organic	
Aqualin	<1
Bromasil	8
Chloropropharm	2
Def	5
Endothall	2
Fluometuron	4
Fluorodifen	1
Folex	3
Herban	2
Maleic hydrazide	3
Ordam	<1
Terbacil	<1
Total	∼33

Total major herbicide production =∼431 million pounds in 1971.

TABLE 5

ESTIMATED MAJOR U.S. INSECTICIDE* PRODUCTION IN 1971[2276,2277]

UNITS IN MILLION POUNDS

Polychlorinated Hydrocarbon		Organophosphorus		Carbamate		Other Organic	
Acaralate	<1	Abate	<1	Bux Ten	6	DBCP	10
Aldrin	10	Aspon	<1	Carbaryl	55	DEET	<1
Chlordane	25	Azodrin	5	Carbofuran	8	Diphacin	<1
Dicofol	4	Bidrin	<1	Total	69	Ethyl hexanediol	<1
Dieldrin	<1	Co Ral	<1			Methomyl	2
DDT	45	Dasanit	4			Methyl bromide	22
Endosulfan	2	Diazinon	10			MGK 264	<1
Endrin	<1	Dichlorvos	<1			MGK 326	<1
Heptachlor	6	Dimethoate	2			Nicotine	<1
Lindane	<1	Dioxathion	<1			Pyrethrins	<1
Methoxychlor	10	Disulfoton	8			Rotenone	<1
Mirex	<1	Dursban	5			Temik	2
Para-dichlorobenzene	60	Dyfonate	2			Tropital	<1
Toxaphen	50	Ethion	2			Warfarin	12
Total	~217	Fenthion	<1			Total	~57
		Guthion	4				
		Malathion	30				
		Meta-Systox R	<1				
		Methyl parathion	45				
		Mevinphos	<1				
		Mocap	<1				
		Naled	2				
		Parathion	15				
		Phorate	8				
		Phosphamidon	<1				
		Ronnel	2				
		Ruelene	2				
		TEPP	<1				
		Trithion	2				
		Zinophos	<1				
		Total	~161				

Total major insecticide production = ~514 million pounds in 1971

* Including miticides, nematocides, rodenticides, molluscicides, fumigants, soil conditioners, etc. The major inorganic insecticides such as arsenates are becoming insignificant as the resu[illegible] strict government controls.

TABLE 6

MAJOR U.S. FUNGICIDE PRODUCTION IN 1971[2276,2277]

UNITS IN MILLION POUNDS

Fungicide	
Benomyl	<1
Captan	18
Chloroneb	<1
Cyprex	2
DCNA	<1
Difolatan	2
Diphenamic	3
Dithio-carbamates	40
Folpet	2
Karathane	<1
PCNB	3
TCP and Salts	20
Total	∿94

Total major fungicide production = ∿94 million pounds in 1971.

TABLE 7

ESTIMATED* PESTICIDE PRODUCTION AND ASSOCIATED PRODUCTION WASTE BY USDA REGION AND STATE[0049,2276,2277]

UNITS, 100 LB/YEAR

USDA Region and State	Herbicide Production	Insecticide Production	Fungicide Production	Herbicide Waste	Insecticide Waste	Fungicide Waste
Region 1, North-Eastern						
New Hampshire	-	-	-	-	-	-
Maine	-	-	-	-	-	-
Vermont	-	-	-	-	-	-
New York	15,200	17,800	3,300	46	53	9.9
New Jersey	19,000	22,200	4,200	57	67	12.6
Pennsylvania	10,100	11,900	1,200	30	36	6.6
Delaware	-	-	-	-	-	-
Maryland	3,800	4,400	800	11	13	2.4
Massachusetts	8,900	10,400	1,900	27	31	5.7
Rhode Island	-	-	-	-	-	-
Connecticut	1,300	1,500	300	3.9	4.5	0.9
Region 2, Appalachian						
Virginia	6,300	7,400	1,400	19	22	4.2
West Virginia	1,300	1,500	300	3.9	4.5	0.9
North Carolina	20,300	23,700	4,400	61	71	13.2
Kentucky	1,300	1,500	300	3.9	4.5	0.9
Tennessee	3,800	4,400	800	11	13	2.4
Region 3, South-Eastern						
South Carolina	6,300	7,400	1,400	19	22	4.2
Georgia	22,800	26,700	5,000	68	80	15.0
Florida	22,800	26,700	5,000	68	80	15.0
Alabama	15,200	17,800	3,300	46	53	9.9
Region 4, Delta States						
Mississippi	11,400	13,300	2,500	34	40	7.5
Arkansas	6,300	7,400	1,400	19	22	4.2
Louisiana	8,900	10,400	1,900	27	31	5.7
Region 5, Corn Belt						
Ohio	12,700	14,800	2,800	38	44	8.4
Indiana	1,300	1,500	300	3.9	4.5	0.9
Illinois	19,000	22,200	4,200	57	67	12.6
Iowa	8,900	10,400	1,900	27	31	5.7
Missouri	11,400	13,300	2,500	34	40	7.5
Region 6, Lake States						
Michigan	8,900	10,400	1,900	27	31	5.7
Wisconsin	8,900	10,400	1,900	27	31	5.7
Minnesota	6,300	7,400	1,400	19	22	4.2
Region 7, Northern Plains						
North Dakota	-	-	-	-	-	-
South Dakota	-	-	-	-	-	-
Nebraska	5,100	5,900	1,100	15	18	3.3
Kansas	5,100	5,900	1,100	15	18	3.3
Region 8, Southern Plains						
Oklahoma	3,800	4,400	800	11	13	2.4
Texas	43,100	50,400	9,400	129	151	28.2
Region 9, Mountain States						
Montana	-	-	-	-	-	-
Idaho	1,300	1,500	300	3.9	4.5	0.9
Wyoming	-	-	-	-	-	-
Colorado	8,900	10,400	1,900	27	31	5.7
New Mexico	-	-	-	-	-	-
Arizona	13,900	16,300	3,000	42	49	9.0
Utah	-	-	-	-	-	-
Nevada	1,300	1,500	300	3.9	4.5	0.9
Region 10, Pacific States						
Washington	10,100	11,900	2,200	30	36	6.6
Oregon	5,100	5,900	1,100	15	18	3.3
California	71,000	83,000	15,500	213	249	46.5

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* These estimations are based on the following assumptions:

(1) Current operational plant sites are those presented in Table 3.

(2) All plant production rates are equal.

(3) An equal herbicide to insecticide to fungicide ratio in all producing states.

(4) Total herbicide, insecticide and fungicide production rates are those presented in Tables 4, 5, and 6.

(5) An average pesticide production waste factor of 3 pounds of waste per 1000 pounds of product.

TABLE 8

MANUFACTURING WASTES FROM THE PRODUCTION OF SELECTED PESTICIDES

Pesticide	Waste Form	Waste Quantity and Distribution	Source
DDT	Aqueous waste containing unknown amount of DDT and Na_2SO_4	68.5 X 10^6 lb/year, Region 10	2501
	Solid waste, unknown amount of DDT	7.7 X 10^6 lb/year, Region 10	2501
Aldrin	Aldrin-containing liquid wastes from spill cleanup and floor washings	Small amount, Region 9	2501
	Solid wastes containing 0.5 % aldrin	2 X 10^6 lb/year, Region 9	TRW Estimate
Dieldrin	Aqueous waste containing dieldrin in ppm range	6.6 X 10^8 lb/year, Region 9	2501
	Solid wastes containing 0.5 % dieldrin	2 X 10^5 lb/year, Region 9	TRW Estimate
Chlordane	Liquid wastes containing approximately 12 % NaCl, 2 % NaOCl, 2 % NaOH and chlordane in ppm range	30 X 10^6 lb/year, Region 5	2293
	Solid wastes containing 0.5 % chlordane	5 X 10^6 lb/year, Region 5	TRW Estimate
Heptachlor	Aqueous waste containing 0.5 ppm heptachlor at pH = 4.0	2.63 X 10^9 lb/year, Region 2	2293
	Liquid residue waste from solvent recovery by distillation	Small amount, Region 2	2293
	Solid wastes containing 0.5 % heptachlor	1.2 X 10^6 lb/year, Region 2	TRW Estimate

TABLE 8 - CONTINUED

MANUFACTURING WASTES FROM THE PRODUCTION OF SELECTED PESTICIDES

Pesticide	Waste Form	Waste Quantity and Distribution	Source
Endrin	aqueous waste containing 0.03 ppm endrin at pH = 11.5	1.71×10^9 lb/year, Region 2	2293
	Liquid residue waste from solvent recovery by distillation	Small amount, Region 2	2293
	Solid Wastes containing 0.5 % endrin	2×10^5 lb/year, Region 2	TRW Estimate
Parathion and Methyl Parathion	Slurry containing parathions and parathion intermediate products such as $(C_2H_5O)_2PSCl$ and $(CH_3O_2)_2$ PSCl	Small amounts, Regions 2, 3, 4, 10	1037
	Solid wastes containing 0.5 % parathions	6×10^6 lb/year, Region 2; 5×10^6 lb/year, Region 3; 6×10^5 lb/year, Region 4; 6×10^5 lb/year, Region 10	TRW Estimate
Demeton and Guthion	Process solution containing 10 % demeton and Guthion and intermediate products in organic solvent	5×10^4 lb/year, Region 5	TRW Estimate
	Solids waste containing 0.5 % demeton and Guthion	10^6 lb/year, Region 5	TRW Estimate

TABLE 8 - CONTINUED

MANUFACTURING WASTES FROM THE PRODUCTION OF SELECTED PESTICIDES

Pesticide	Waste Form	Waste Quantity and Distribution	Source
	Still bottoms containing 2,4-D, 2,6-D and chlorophenols	Small amounts, Regions 4, 6, 10	2501
2,4-D	Solid wastes containing 0.5 % 2,4-D	6 X 10^5 lb/year, Region 4; 7 X 10^6 lb/year, Region 6; 6 X 10^5 lb/year, Region 10	TRW Estimate

TRW estimates on solid wastes (contaminated rags, bags, filter solids, fiber drums, steel drums, etc) are based on 0.2 lb solid waste generated per lb of pesticide active ingredient produced. TRW estimate on process solution wastes is based on 0.01 lb liquid waste per lb of pesticide active ingredient produced.

TABLE 9

ESTIMATED* MANUFACTURING WASTES FROM THE FORMULATION OF SELECTED PESTICIDES
UNITS - ACTIVE INGREDIENT (LB/YEAR)

	USDA REGIONS										
Pesticide	1	2	3	4	5	6	7	8	9	10	Total
DDT	500	2,200	9,800	5,400	800	400	-	3,700	600	1,600	25,000
Lindane	-	210	530	-	-	-	-	130	-	130	1,000
Aldrin	-	1,000	200	-	7,700	700	400	-	-	-	10,000
Dieldrin	170	50	230	-	140	80	60	80	190	-	1,000
Chlordane	-	2,300	-	-	19,600	2,100	1,000	-	-	-	25,000
Heptachlor	-	600	-	-	4,700	500	200	-	-	-	6,000
Endrin	-	80	230	430	-	-	-	110	-	150	1,000
Parathion	930	630	2,720	-	-	-	1,640	3,610	1,310	4,160	15,000
Methyl Parathion	-	-	9,000	24,300	-	-	-	11,700	-	-	45,000
Guthion	840	180	620	-	260	390	-	-	-	1,710	4,000
Demeton	40	130	-	-	-	-	-	50	-	780	1,000
2,4-D	1,700	1,300	800	1,000	9,400	3,900	10,300	2,700	6,900	7,000	45,000

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* These estimates are based on the following assumptions:

(1) 0.02 lb organic liquid waste containing 5 percent pesticide active ingredient per lb of pesticide active ingredient formulated;

(2) the quantity of a pesticide formulated in a region is proportional to the quantity of the pesticide used on crops in that region.

The waste generation factor for contaminated solvents from pesticide formulation was computed with the following assumptions: (1) a 40 percent active ingredient concentration for formulated liquid pesticides;[0619] (2) three organic solution rinses of 40 gal. each are used in process equipment cleanup for every 1,500 gal. of liquid pesticide formulated[*];[2501] (3) a 0.1 percent active ingredient loss in the liquid pesticide formulation process; and (4) 90 percent of the organic solutions used for cleanup purposes are evaporated[†] from the sumps before the liquid wastes are removed for disposal.

The quantity of process solution wastes generated from pesticide production varies from negligible amounts to several times the quantity of pesticide active ingredient produced, depending on the chemical reactions involved and the subsequent purification steps employed. The composition of the process solution wastes, for the same reasons, is equally difficult to characterize, although the organic solution containing 10 percent pesticide active ingredients represents a fairly typical process waste stream (Table 1). The waste generation factor of 0.01 lb process solution waste per lb of pesticide active ingredient produced was computed from the balance of the other two pesticide production wastes, to make up for a total of 3 lb of pesticide active ingredient loss per 1,000 lb of pesticide active ingredient produced, as indicated previously.

Empty Pesticide Containers and Residual Pesticide Wastes

Although the number of empty pesticide containers throughout the United States has been growing every year, current information on the numbers and sizes of empty pesticide containers is not readily available.

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[*] Liquid pesticide formulation normally involves mixing in 1,500 gal. size tanks.

[†] As a result of the evaporation process, the liquid wastes removed are ten times more concentrated in the pesticide active ingredients than the original cleaning solutions. Thus, the final pesticide active ingredient concentration of the liquid waste could reach as high as 3o to 40 percent, although the average is closer to 5 percent (Table 1).

Reasonable estimates on the numbers and types of pesticide containers and the quantity and regional distribution of pesticide residues, however, could be made by using the following information:

(1) data on the weighed percentage estimates of active pesticide ingredients, proportional usage, and packaging sizes for formulated pesticides by class and formulation types (Table 10) developed by Jansen[0619];

(2) data on the total 1970 domestic fungicide, herbicide, and insecticide use given in Pesticide Review [1738];

(3) data from a University of California, Davis study indicating that liquid residues left in pesticide containers are 400 gm for the 55-gal. container, 40 gm for the 5-gal. container, and 14 gm for the 1-gal. container[2592];

(4) the assumption that the quantity of pesticide residues left in empty dry packages and aerosol cans is small compared to the quantity of pesticide residues left in liquid pesticide containers;

(5) the assumption that the regional distribution of pesticide residues is proportional to the quantity of each pesticide used on crops in that region.[0449]

The total number of pesticide containers of all sizes in 1970 has been computed to be in excess of 199 million (Table 11). Of these, approximately 30 million are liquid pesticide containers which pose the greatest disposal problem.

The total quantity of pesticide active ingredients in empty containers has been estimated to be 868,000 lb in 1970 (Table 12). To indicate the significance of these pesticide residue wastes, the estimated 136,000 lb organophosphorus insecticide residue is sufficient to cause the death of 35 million people if taken internally.[*]

Surplus Pesticides Stored in Government Facilities

Sizable quantities of surplus pesticides have been accumulated in recent years due to the cancellation of certain use patterns. The most significant of these to date has been DDT. Since then, suspension or

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[*] By assuming an acute oral LD_{50} of 14 mg/kg for the organophosphorus insecticides.

TABLE 10

WEIGHED PERCENTAGE ESTIMATES OF ACTIVE PESTICIDE INGREDIENTS, PROPORTIONAL USAGE, AND PACKAGING SIZED FOR FORMULATED PESTICIDES BY CLASS AND FORMULATION TYPES

Pesticide Class and Formulation Type	Active Ingred-ient	Propor-tional Use	Package Sizes*		
			Large	Inter-mediate	Small
	%	%	%	%	%
Fungicides					
Liquid	23.8	46.9	78	15	7
Dry	33.7	53.1	16	--	84
Herbicides					
Liquid	43.5	55.5	31	52	17
Dry	19.3	44.5	75	--	25
Insecticides					
Liquid	35.9	70.5	42	40	18
Dry	9.2	26.6	53	--	47
Aerosol	98.0	2.9	--	--	100

Liquid	55-gal	5-gal	1-gal
Dry	50-lb		4-lb
Aerosol			1-lb

TABLE 11
ESTIMATED DISTRIBUTION OF PESTICIDE CONTAINERS BY SIZE AND TYPE IN 1970

	Package Size						
	Liquid			Dry		Aerosols	
Class of Pesticides	55-gal. (1,000)	5-gal. (1,000)	1-gal. (1,000)	50-lb (1,000)	1-lb (1,000)	1-lb (1,000)	Total (1,000)
Fungicides	279.44	591.13	1,373.71	403.33	26,469.27	-	29,116.88
Herbicides	281.09	5,186.57	8,478.06	10,815.02	45,062.59	-	69,832.33
Insecticides and Others	404.40	4,236.68	9,532.52	6,611.96	73,292.96	6,384.13	100,462.65
Total by Size	964.93	10,014.38	19,383.69	17,830.31	144,824.82	6,384.13	199,402.86

TABLE 12

ESTIMATED QUANTITY OF PESTICIDE RESIDUE LEFT IN EMPTY CONTAINERS UNITS - ACTIVE INGREDIENT (LB/YEAR)

Pesticide Type and Category	USDA REGIONS 1	2	3	4	5	6	7	8	9	10	Total
Herbicides											
Inorganic	7,280	4,220	1,450	2,550	750	-	400	1,500	11,390	810	30,350
Benzoic	-	-	480	1,450	55,680	7,750	5,330	-	730	13,560	84,980
Triazine	14,850	12,210	1,320	330	32,350	30,200	7,430	1,160	160	1,160	101,170
Phenyl-urea	1,390	1,110	1,390	5,570	1,390	420	20	560	40	1,260	13,150
Phenoxy	1,830	1,710	1,600	1,510	10,140	4,650	11,910	3,450	7,250	7,540	51,590
Dinitro	15,540	2,120	7,070	-	710	530	-	90	180	5,100	31,360
Chlorinated Aliphatic	6,170	-	-	1,700	1,230	4,630	2,160	150	-	150	16,190
Organic Arsenical	-	260	390	27,040	-	-	-	7,720	-	-	35,410
Carbamate	20	320	450	2,190	7,720	1,010	400	6,500	400	1,220	20,230
Other Organic	480	5,740	5,740	4,310	13,640	2,150	240	1,430	480	1,200	35,410
Insecticides											
Inorganic	2,840	2,130	260	-	450	1,160	-	4,200	-	710	11,750
Polychlorinated Hydrocarbons	910	5,630	16,060	11,100	980	6,880	360	6,970	1,280	2.330	52,500
Organophosphorus	5,910	6,780	18,950	26,080	2,430	7,650	9,390	23,820	6,610	28,340	135,960
Other Organic	24,710	14,000	32,940	23,880	9,060	6,180	410	24,710	2,880	28,420	167,190
Fungicides											
Organic and Inorganic	3,900	10,100	35,600	100	3,800	2,100	150	2,900	600	21,500	80,750
Total Pesticides	85,830	66,330	123,700	107,810	140,330	75,310	38,200	85,160	32,000	113,320	867,990

cancellation of certain uses of 2,4,5-T, several mercury compounds, aldrin, dieldrin, etc., has been effected, and this has contributed to the disposal problem.

Surplus pesticides are currently stored in Department of Defense facilities and state/Environmental Protection Agency (EPA) regional facilities. Information on the quantities, types and locations of surplus pesticides was obtained from the Defense Supply Agency and EPA sources,[2222] and the data has been summarized and separately tabulated for Department of Defense surplus pesticides and state/EPA surplus pesticides (Tables 13, 14, 15). The quantity of surplus pesticides currently in storage in Department of Defense facilities in the continental United States awaiting disposal amounts to 10 million lb, including 8.2 million lb phenoxy herbicides, 1.4 million lb polychlorinated hydrocarbon insecticides, and 140,000 lb organophosphorus insecticides. The quantity of surplus pesticides under the custody of the regional Environmental Protection Agency offices and requiring disposal amounts to 1.8 million lb. In addition, there are also 25,000 55-gal. drums of 2,4-D and 2,4,5-T manufacturing by-product wastes stored at Alkali Lake, Oregon.

TABLE 13

DEPARTMENT OF DEFENSE SURPLUS ORGANIC PESTICIDE SURVEY$^{(a)}$
UNITS, LB TOTAL - LB ACTIVE INGREDIENT

USDA REGION AND STATE(b)	HERBICIDES						INSECTICIDES			FUNGICIDES	Approximate Total Pesticides
	Benzoic	Phenyl-Urea	Phenoxy	Chlorinated Aliphatic	Carbamate	Other Organic	Polychlorinated Hydrocarbons	Organo-Phosphorus	Other Organic	Organic	
Region 1											
North-Eastern											
New york	450 - 450						90,000 - 9,200	100 - 50		150-130	90,000- 9,000
New Jersey							1,100 - 800				1,100- 800
Pennsylvania		1,100 - 900	1,200 - 1,100				32,700 - 30,200				35,000-32,000
New Hampshire							430 - 100				400- 100
Maryland				951 - 850			1,550 - 1,550				1,700- 1,600
Massachusetts			80 - 80				700 - 50				800- 150
Washington D.C.							4,800 - 1,100				4,800- 1,100
Region 2											
Appalachian											
Virginia	350 - 280	120 - 100	1,200 - 1,000	300 - 260			98,700 - 35,100	1,900- 500			92,900-37,300
North Carolina							55,300 - 13,200		750- 750		56,000-14,000
Tennessee							39,000 - 15,300				39,000-15,300
Region 3											
South-Eastern											
South Carolina							120 - 20				120- 20
Georgia	1,200 - 1,200	700 - 200	4,500 - 4,500	3,100 - 2,600		2,000 - 2,000	69,400 - 11,100	4,500-4,300	7,400- 7,300		92,800-33,400
Florida			2,000 - 1,600	50 - 40		5,000 - 2,500	58,500 - 20,100				65,500-24,200
Alabama							1,900 - 1,400	25- 1			1,900- 1,400
Region 4											
Delta States											
Mississippi			6,354,000 - 6,815,000				5,100 - 1,100				6,959,000-6,816,000
Arkansas		120 - 120									120- 120
Region 5											
Corn Belt											
Ohio							2,600 - 160				2,600- 160
Indiana	25 - 20		570 - 570	130 - 110	200 - 120		300 - 80	840- 340	350- 350		2,500- 1,600
Illinois			5,000 - 5,000				19,900 - 3,000				20,400- 8,000
Missouri							1,900 - 1,800	500- 80			2,400- 1,900
Region 6											
Lake States											
Michigan							1,600 - 850				1,600- 850
Region 7											
Northern Plains											
South Dakota						50 - 1	2,000 - 100		60 - 60		2,100- 160
Nebraska							70 - 10				70- 10
Kansas							60 - 30				60- 30
Region 8											
Southern Plains											
Oklahoma							210 - 20				210- 20
Texas			1,222,000 - 1,161,000	50 - 40			44,600 - 7,300				1,267,000-1,168,000
Region 9											
Mountain States											
Wyoming							160 - 90	250- 130			410- 220
Colorado					120 -		12,400 - 3,300	500- 10			13,000- 3,400
New Mexico	60 - 50		1,600 - 1,600	75 - 60			170 - 80				1,900- 1,800
Arizona	600 - 500		50 - 40				2,800 - 700				3,400- 1,200
Utah				200 - 200			7,200 - 1,600	1,250- 660			8,700- 2,500
Region 10											
Pacific States											
Washington							37,300 - 3,100	10-5			37,300- 3,100
Oregon							353,500 - 30,800		20,000-20,000		373,500-50,800
California							377,600 - 65,500	30,100-25,000			369,100-90,500
Alaska			2,900 - 2,900			1,200 - 10	15,500 - 10,300	98,000-73,000	200- 2		116,400-86,200
Hawaii							18,800 - 1,100				18,800- 1,100

(a) Basic data obtained from Department of Defense inventory of pesticide wastes.2222
Liquid pesticide density assumed equal to water density.
When no active ingredient concentration data available, 100 percent assumed.

(b) States not listed in appropriate USDA regions contain no DOD pesticide wastes.

TABLE 14

DEPARTMENT OF DEFENSE SURPLUS INORGANIC PESTICIDE UNITS, LB TOTAL - LB ACTIVE INGREDIENT

USDA Region and State	Herbicides	Insecticides	Fungicides	Total Pesticides
Region 1				
North-Eastern				
New York		300 - 300		300 - 300
New Jersey		5 - 5	100 - 100	105 - 105
Pennsylvania	12,000 - 12,000			12,000 - 12,000
Region 2				
Appalachina				
Virginia		20 - 14		20 - 14
Region 3				
South-Eastern				
Georgia		537 - 470		537 - 470
Florida		31,100 -2,600		31,100 -2,600
Region 4				
Delta States				
Louisiana		60 - 60		60 - 60
Region 5				
Corn Belt				
Indiana			10 - 0.3	10 - 0.3
Illinois		650 - 650	25 - 25	675 - 675
Missouri		10 - 10	110 - 110	120 - 120
Region 6				
Lake States				
Michigan		16 - 15		16 - 15
Region 8				
Southern Plains				
Texas		1,624 -1,591		1,624 -1,591
Region 9				
Mountain States				
New Mexico		6 - 6		6 - 6
Region 10				
Pacific States				
Washington		25,500-25,500		25,500 - 25,500
Oregon		160- 160		160 - 160
California		4,550- 4,550		4,550 - 4,550
Alaska		16,200-16,200	1,200 - 960	17,400 - 17,160

TABLE 15

SURPLUS PESTICIDES STORED BY VARIOUS STATES AND EPA REGIONAL OFFICES

USDA Region and State	Types and Quantities of Pesticides in Storage
Region 1	
New Hampshire	3 to 5 tons of unidentified pesticides
Rhode Island	Small amount of DDT
New Jersey	1 ton of fire damaged pesticides, principally organophosphates, chlorinated hydrocarbons, and carbamates
New York	1,000,000 lb of assorted pesticides, 100,000 lb of water damaged pesticides including dieldrin
Delaware	Small amounts of pesticides
Region 2	
Virginia	115 tons of pesticides
North Carolina	82 tons of DDT and DDT-Parathion mixtures
Region 3	
Florida	86,000 lb mixed pesticides 3,360 lb Parathion 2,100 lb Chlordane
Georgia	800 lb drum spray 5,950 lb DDT-BHC-Trithon 3,840 lb DDT-BHC 3,810 lb DDT-BHC Ethion 2,850 lb Chlordane-BHC-DDT 2,460 units Harris Ant Buttons (Arsenate) 1,428 units Tick Spray 1,351 containers DDVP Strips 8,360 lb Veon-245 5,600 lb Disinfectant
Region 5	
Indiana	Unknown quantities of pesticides
Region 6	
Minnesota	Unknown quantities of pesticide wastes
Michigan	111,228 lb of material containing 27,065 lb of DDT

TABLE 15 - CONTINUED

SURPLUS PESTICIDES STORED BY VARIOUS STATES AND EPA REGIONAL OFFICES

USDA Region and State	Types and Quantities of Pesticides in Storage
Region 10	
Alaska	13,400 lb of technical DDT
	575 lb of technical chlordane
	100 lb of technical toxaphene
	300-500 lb of insoluble complex of copper-chromium-arsenic
Oregon	13,750,000 lb of 2,4-D and 2,4,5-T manufacturing by-product
	1,200 lb of arsenic trioxide
	1,000 lb of 10 % DDT
	104 lb of Parathion
Washington	96 lb of 95 % lead arsenate
	305 lb of 70 % calcium arsenate
	50 lb of 5 % chlorthion
	32 lb of 27 % Phosdrin
	25 lb of technical grade mercury cyanide

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WASTES OF MERCURY AND MERCURY COMPOUNDS

The principal sources of mercury wastes in solid, semi-solid or concentrated liquid forms have been identified as (1) brine sludges from mercury cell chlor-alkali plants; (2) waste sludges from paint manufacturers; (3) paint residue left in used paint containers; and (4) mercury used in electrical apparatus, industrial and control instruments, etc. that are not currently recycled. In addition, there are also small quantities of surplus mercury and mercury compounds stored in Department of Defense and regional Environmental Protection Agency facilities (Table 1).

The constituents of the brine sludges from mercury cell chlor-alkali plants include barium sulfate, calcium carbonate, calcium sulfate, magnesium oxide, magnesium hydroxide, graphite, some iron, aluminum, mud, rocks, and typically 100 ppm mercury in the form of $HgCl_4^=$. An estimated 16,500 lb of mercury are lost through 56,800 tons of brine sludges per year (Table 1). A detailed discussion of the mercury containing brine sludges is included in a later section of this report.

Phenyl mercury compounds are still used as mildewcides in water-based paints in concentrations of 0.004 to 0.1 percent (as mercury). Phenyl mercuric acetate, phenyl mercuric oleate, and di(phenyl mercuric) dodecenyl succinate represent the three types most commonly employed as paint additives. Solid wastes are generated from the manufacture of paint and allied products as a result of kettle washings and equipment cleanup. In the latex washing system, the waste sludges typically contain 15 percent pigments, 20 percent binders, 65 percent water, and 100 to 150 ppm mercury. It is estimated that 1,800 lb of mercury are lost through 26 million lb of water-based paint sludges every year. The geographical distribution of these waste paint sludges was calculated on the basis of the distribution of "value added by manufacture" dollar amounts for paints and allied products and by Bureau of Census regions (Table 1). A more complete discussion of the sources and constituents of the mercury containing wastes from paint manufacture, along with the assumptions used in the computation of the total quantity of the wastes, can be found in the report "Toxic Paint Wastes."

TABLE 1

WASTES OF MERCURY AND MERCURY COMPOUNDS

Source and Material	Bureau of Census Regions									
	I	II	III	IV	V	VI	VII	VIII	IX	Total
	Annual Waste Production (lb/year)									
Brine Sludge										
Mercury	110	3,120	1,010	-	1,385	3,260	5,510	-	2,115	16,510
Sludge	1.1×10^6	31.2×10^6	10.1×10^6	-	13.9×10^6	44.7×10^6	8.9×10^6	-	3.7×10^6	113.6×10^6
Paint Sludge										
Mercury	45	395	555	120	155	85	135	20	290	1,800
Sludge	0.65×10^6	5.74×10^6	7.99×10^6	1.70×10^6	2.23×10^6	1.24×10^6	1.93×10^6	0.31×10^6	4.21×10^6	26.0×10^6
Paint Residue										
Mercury	1,900	6,000	6,500	2,400	5,000	2,100	3,100	1,400	4,300	32,700
Old paint	13×10^6	41×10^6	44×10^6	16×10^6	34×10^6	14×10^6	21×10^6	9×10^6	29×10^6	221×10^6
Mercury from electrical apparatus, industrial and control instruments, etc.	5.8×10^4	18.4×10^4	20.0×10^4	7.4×10^4	15.2×10^4	6.3×10^4	9.6×10^4	4.1×10^4	13.2×10^4	100.0×10^4
	Stored Wastes (lb)									
Mercury	-	3,700	25	9.5	-	-	-	-	-	3,735
Mercuric Nitrate	-	-	-	-	-	-	-	-	5	5
Mercuric and mercurous chloride	100	-	-	110	-	-	-	-	-	210
Mercuric Cyanide	-	-	-	-	-	-	-	-	25	25

The paint residues left in used paint containers discarded in municipal dumps often contain 0.02 to 0.10 percent mercury and is another major source of mercury waste. It is estimated that as much as 32,700 lb of mercury are lost through these paint residues per year. The geographical distribution of these paint residue wastes was calculated on the basis of the population distribution in the United States (Table 1). Again, a more complete discussion of the paint residue wastes can be found in the report "Toxic Paint Wastes".

Of the mercury used for other potentially recyclable uses, such as electrical equipment, measurement and control apparatus, and general laboratory uses, approximately 1 million lb per year (in batteries, fluorescent tubes, switches, etc.) are disposed of in landfills, dumps and incinerators. This was estimated by assuming that only 44 percent of the 1,800,000 lb of mercury consumed for these purposes in 1971 were actually recycled.[2105] The geographical distribution of these mercury wastes was calculated on the basis of the population distribution in the United States (Table 1).

Mercury compounds in relatively low levels are also found in the liquid effluents from pharmaceutical and battery manufacturing plants. The mercury compounds present are usually either reduced to metallic mercury by the use of sodium borohydride (or zinc) or precipitated as mercuric sulfide by the addition of sodium sulfide, and then collected by filtration and reclaimed for their mercury value. Mercury wastes from these manufacturers are therefore insignificant.

Mercury Containing Brine Sludges from the Mercury Cell Chlor-Alkali Plants

Approximately 25 percent of the U.S. supply of chlorine comes from mercury cells, which produce a higher grade caustic soda that is highly concentrated and essentially free of chlorine impurities. The total chlorine capacity of mercury cells in the United States is about 7,000 tons per day from 29 installations around the country*, with plant capacities ranging from 6 to about 700 tons per day. In the mercury cell process, a circulating sodium chloride solution is electrolyzed in the cell in which mercury serves as the cathode; the anode is usually graphite. Sodium ion reacts with mercury to form an amalgam, and chlorine gas is produced at the anode. The mercury flows through the cell, picking up sodium on the way, and is pumped to a regeneration cell, where the amalgam is mixed with water and forms one-half of a self-shorted electrolytic cell, with iron serving as the other electrode. The regeneration cell removes sodium from the amalgam and produces caustic soda (approximately 50 percent solution) and hydrogen gas. The regenerated mercury is then returned to the mercury cell and the process is repeated. The brine solution leaves the mercury cell and is vacuum de-chlorinated and then purged with air to remove the last of the chlorine. The solution is then saturated with salt, and this is followed by a purification step, in which various impurities from the newly added salt are precipitated. The brine is then passed through a filter and back to the mercury cell.

For resaturation of the partly depleted brine from electrolysis, solid salt is required by the mercury cell process. If only brine is available, this must be evaporated first to produce solid salt. Typical sources of salt include shaft mined rock salt, vacuum pan salt, solar pond salt, and salt recovered from the cell liquor evaporator in an adjacent diaphragm cell plant. The ideal raw material for the mercury cell process is, of course, highly purified recrystallized salt with a purity of 99.99 + percent NaCl.

If the salt feed is of extremely high purity, the brine need only be filtered before returning it to the cells. If salt recovered from the diaphragm cell caustic evaporators is used, brine purification normally involves the addition of caustic soda followed by filtration, the sludge obtained is mainly graphite, along with some $CaCO_3$, $Mg(OH)_2$, and iron. When either high purity recrystallized salt or recovered salt from the diaphragm cell caustic evaporator is used, smaller quantities of mercury containing brine sludges are generated. These can often be treated and disposed of safely on the property.

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*Five of the installations also have diaphragm cell chlorine plants at the same location.

If rock salt or solar salt is used, the full brine stream is treated for the removal of Mg, Fe, $CaCl_2$ and $CaSO_4$ equivalent to the pickup from the salt dissolved. Brine purification includes the addition of barium carbonate to remove sulfates, the addition of sodium carbonate or carbon dioxide to precipitate calcium, the addition of caustic soda to remove magnesium and heavy metals, and the addition of flocculents to cause settling of the precipitates. Depending on the impurities initially present in the salt, the constituents of the brine sludge include barium sulfate, calcium carbonate, calcium sulfate, magnesium cxide, magnesium hydroxide, graphite, some iron, aluminum, mud, rocks, and typically 100 ppm mercury in the form of $HgCl_4^{=}$. Mercury losses through the brine sludges from the mercury cell chlor-alkali plants range from 0.001 to 0.04 lb per ton of chlorine produced. The mercury containing brine sludges are currently being pumped into settling basins awaiting the development and installation of adequate treatment processes.

The location, producer, chlorine production capacity, the rate of brine sludge production, and the rate of mercury loss through the brine sludges of all the 29 mercury cell chlorine plants in the United States have been summarized (Table 2). In addition, the annual chlorine production capacity, the annual mercury loss through brine sludges, and the annual brine sludge production by state are also presented (Table 3). The data used in both tables were obtained through contacting the individual chlor-alkali plants.[2643-2662,2664]

TABLE 2

MERCURY LOSSES THROUGH BRINE SLUDGES FROM MERCURY CELL CHLOR-ALKALI PLANTS

State & City	Producer	Chlorine Production Capacity (tons/day)	Source of Salt	Mercury Loss Through Brine Sludges (lb/day)	Quantity of Brine Sludges Produced (tons/day)
Alabama					
Le Moyne	Stauffer Chemical Co.	190	Rock Salt, 99% NaCl	0.15	2.5
McIntosh	Olin Corp.	350	Rock Salt (high purity)	-	-
Mobile	Diamond Shamrock	100	Rock Salt	0.25 - 1.50	2
Muscle Shoals†	Diamond Shamrock	285	?	1.88	9.4
Delaware					
Delaware City†	Diamond Shamrock	400	?	2.64	13.2
Georgia					
Augusta†	Olin Corp.	390	?	2.52	12.6
Brunswick	Allied Chemical Corp.	285	Recrystallized solar pond salt	-	-
Illinois					
East St. Louis	Monsanta Co.	100	?	0.66	3.30
Kentucky					
Calvert City	B. F. Goodrich Chemical Corp.	330	Rock Salt	1.1	11.7
Calvert City	Pennwalt Corp.	300	Rock Salt	1.35	21
Louisiana					
Geismar	BASF Wyandotte Corp.	110	recovered salt from diaphragm cell caustic liquor	0.7	0.25
Lake Chalres	PPG Industries, Inc.	700	Recovered salt from diaphragm cell caustic liquor	-	-
St. Gabriel	Stauffer Chemical Co.	430	Rock Salt, 99.1% NaCl	14.4	12

TABLE 2 - CONTINUED

MERCURY LOSSES THROUGH BRINE SLUDGES FROM MERCURY CELL CHLOR-ALKALI PLANTS

State & City	Producer	Chlorine Production Capacity (tons/day)	Source of Salt	Mercury Loss Through Brine Sludges (lb/day)	Quantity of Brine Sludges Produced (tons/day)
Maine					
Orrington	Sobin Chlor-Alkali Inc.	160	Solar pond salt	0.18 - 0.30	1.50
New Jersey					
Linden[+]	Linden Chlorine Products	500	Rock Salt	3.32	16.6
New York					
Niagara Falls[*]	Hooker Sobin Chemical	140	?	0.92	4.6
Niagara Falls[+]	Olin Corp.	250	Rock salt	1.66	8.3
Syracuse	Allied Chemical Corp.	250	Recovered salt from diaphragm cell caustic liquor	-	-
North Carolina					
Acme	Allied Chemical Corp.	165	Recovered salt from diaphragm cell caustic liquor	-	-
Pisgah[*]	Olin, Ecusta Operations	6	Rock Salt, 99% purity	0.02	0.1
Ohio					
Ashtabula[*]	Detrex Chemical Industries	60	Mined salt, 98% purity	0.40	2
Tennesse					
Charleston[†]	Olin Corp.	455	?	2.96	14.8
Texas					
Deer Park	Diamond Shamrock	250	Recovered salt from diaphragm cell caustic liquor	-	-
Point Comfort	Aluminum Co. of America	400	Evaporated salt (NaCl > 99.9%)	-	-
Washington					
Bellingham	Georgia-Pacific Corp.	135	Solar pond salt	5	1
Longview[*]	Weyerhaeuser Co.	265	Solar pond salt	0.80	4

TABLE 2 - CONTINUED

MERCURY LOSSES THROUGH BRINE SLUDGES FROM MERCURY CELL CHLOR-ALKALI PLANTS

State & City	Producer	Chlorine Production Capacity (tons/day)	Source of Salt	Mercury Loss Through Brine Sludges (lb/day)	Quantity of Brine Sludges Produced (tons/day)
West Virginia					
Moundsville	Allied Chemical Corp.	250-300	Purified evaporated salt	-	-
New Martinsville[+]	PPG Industries Inc.	190	?	1.26	6.3
Wisconsin					
Port Edwards	BASF Wyandotte Corp.	168	97-98% NaCl Salt from Detroit	1.7	8.5

- Means both mercury loss and brine sludge production are negligible because highly purified salt is used.

[+] When insufficient data is supplied, the quantity of brine sludges produced is estimated on the basis that the salt is 98 percent NaCl. The mercury loss through brine sludges is estimated by assuming that the mercury in the brine sludges is 100 ppm.

[*] The mercury loss is estimated by assuming that the mercury concentration in the brine sludge is 100 ppm.

TABLE 3

REGIONAL DISTRIBUTION OF MERCURY CONTAINING BRINE SLUDGE PRODUCTION

State	Annual Chlorine Capacity (Tons)	Annual Mercury Loss (lb)	Annual Production of Brine Sludge (Tons)
Alabama	337,600	1,288	5,070
Delaware	146,000	964	4,820
Georgia	250,000	920	4,600
Illinois	36,500	241	1,200
Kentucky	230,000	894	11,900
Louisiana	452,600	5,512	4,470
Maine	58,400	110	550
New Jersey	182,500	1,212	6,060
New York	233,600	942	4,710
North Carolina	62,400	7	40
Ohio	21,900	146	730
Tennesses	166,000	1,080	5,400
Texas	237,000	-	-
Washington	146,000	2,117	1,825
West Virginia	178,000	460	2,300
Wisconsin	61,300	621	3,100
Total	2,799,800	16,514	56,775

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WASTES OF ARSENIC AND ARSENIC COMPOUNDS

The principal sources of arsenic wastes have been identified as: (1) flue dust from coal combustion; (2) flue dust from metal smelters; (3) production of food grade phosphoric acid; (4) pesticide manufacture and pesticide residues left in used containers; and (5) surplus arsenic pesticides in storage and arsenic contaminated soil. Detailed discussions of the quantities, forms, composition, and geographical distribution of the arsenic containing waste streams from these sources are included in the following sections of this report.

Arsenic Wastes from Coal Combustion

Coal contains 0.8 to 16 micrograms of arsenic per gram of coal and for this reason the air of most large cities contains a small amount of arsenic, probably as arsenic trioxide. Based upon the average arsenic content of coal and a 400 million ton annual consumption of coal,[0634] the total quantity of arsenic trioxide emitted from coal combustion amounts to 8.5 million lb per year. The fraction of this amount that is being trapped by particulate removal systems is difficult to estimate, but is expected to increase as tighter emission standards are enforced. The form that this waste material is likely to take depends on the scrubbing method, but in any case, the particulate residues will consist mainly of calcium oxide, iron oxide, and other oxides. The geographical distribution of the arsenic wastes from coal combustion was calculated on the basis of the regional distribution of coal fired power plants in the United States (Table 1).

Arsenic Wastes from Metal Smelting

Arsenic is present, normally as the sulfide, in most of the copper, lead, zinc and other ores that are processed in the United States. In the smelting of the metals, arsenic is oxidized to the more volatile arsenic trioxide which exits up the flue stacks where most of it is recovered.

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TABLE 1

WASTES OF ARSENIC AND ARSENIC COMPOUNDS

Source and Material	Bureau of Census Regions									
	I	II	III	IV	V	VI	VII	VIII	IX	Total
	Annual Waste Production (lb/year)									
Coal combustion, as As_2O_3	0.14×10^6	1.25×10^6	3.21×10^6	0.61×10^6	1.72×10^6	1.27×10^6	-	0.30×10^6	-	8.50×10^6
Metal smelting as As_2O_3	-	0.6×10^6	0.3×10^6	2.1×10^6	0.1×10^6	0.2×10^6	2.4×10^6	16.7×10^6	1.6×10^6	24.0×10^6
Production of food grade phosphoric acid, as As_2S_3	0.2×10^4	0.8×10^4	1.0×10^4	0.2×10^4	0.2×10^4	0.2×10^4	0.4×10^4	0.2×10^4	0.8×10^4	4.0×10^4
Pesticide residue in used paint containers, as active ingredient	-	-	-	-	-	0.9×10^4	2.6×10^4	-	-	3.5×10^4
	Stored Waste (lb)									
As_2O_3 from metal smelting	-	-	-	-	-	-	-	-	4×10^7	4×10^7
Cacodylate contaminated solid waste (1.5% cacodylate)	-	-	6×10^7	-	-	-	-	-	-	6×10^7

TABLE 1 - CONTINUED

WASTES OF ARSENIC AND ARSENIC COMPOUNDS

Source and Material	Bureau of Census Regions									
	I	II	III	IV	V	VI	VII	VIII	IX	Total
Still bottom residue (15% As)	-	-	-	-	-	-	-	-	1.6×10^4	1.6×10^4
Lead arsenate	-	-	12	-	-	-	1,600	-	24,100	25,712
Calcium arsenate	-	-	-	-	-	-	-	-	214	214
Sodium arsenite	-	150	325	-	550	-	-	-	8,100	9,125
Copper acetoarsenite	-	-	-	-	1,500	-	-	-	-	1,500

American Smelting and Refining Company (ASARCO) at Tacoma, Washington is the largest producer of arsenic trioxide and until recently has acted as a single point processing agent for the arsenic trioxide containing flue dusts from virtually every smelter in the United States.* ASARCO recovers 800 to 1,000 tons of arsenic trioxide per month from flue dusts normally containing about 30 percent arsenic trioxide.[1559] Assuming that ASARCO has almost 100 percent efficiency in arsenic trioxide recovery, the amount of arsenic trioxide contained in the flue dusts received by ASARCO would be approximately equal to the amount of arsenic trioxide recovered. This indicates that the total quantity of arsenic containing flue dusts collected from the smelting of copper, lead, zinc and other arsenic-bearing ores amounts to 80 million lb per year.

In addition to the crude arsenic trioxide, the flue dusts from metal smelting contain mineral oxides, silica, and other materials. The geographical distribution of the 24 million lb of arsenic trioxide contained in these flue dusts was calculated on the basis of the regional distribution of copper, lead, and zinc refineries in the United States and by Bureau of Census regions (Table 1). At the present time, as the result of low market demand, there is also a stockpile of estimated 40 million lb of arsenic trioxide at ASARCO's Tacoma Site.

Arsenic Wastes from Phosphoric Acid Production

Nearly all phosphate rocks contain arsenic to some extent. Low level arsenic wastes are generated from the production of phosphoric acid by either the wet process or the furnace method, but these are of little concern and can be safely disposed of into lagoons or landfills. In the purification of the crude phosphoric acid to yield the food grade product, however, arsenic wastes of much higher concentrations are obtained.

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*These smelter flue dusts are sent to ASARCO for reclamation of their metal values.

The wastes from the wet process consist of a slurry of spent gypsum, aluminum and iron phosphate sludges as well as the residual arsenic. The arsenic content can be expected to range widely but is estimated to average 6 ppm as arsenic.* In addition, the spent, extracted rock also contains residual amounts of arsenic.

The wastes from the furnace process consists primarily of spent rock from the thermal reduction. Most of the arsenic in the rock is reduced to the element and is recovered along with the elemental phosphorus. The subsequent burning of the phosphorus creates only small quantities of wastes and most of the arsenic is carried over with the resultant P_2O_5 and is thereby included in furnace grade acid.

Approximately 500 million lb of phosphoric acid, primarily the furnace grade product (50 ppm As), are annually treated for arsenic removal to yield the food grade product. Hydrogen sulfide is bubbled through the acid to precipitate the highly insoluble arsenic sulfide,[2587] and a typical waste stream from this process contains 8 percent arsenic sulfide, 7 percent activated carbon, 29 percent filter acid, 35 percent phosphoric acid, and water.† Based on an arsenic concentration of 50 ppm in the furnace acid, it is estimated that approximately 40,000 lb of arsenic sulfide are produced annually from this purification step. The geographical distribution of these arsenic wastes was calculated on the basis of the industry information on cities in which purification is performed (Table 1).[2587]

Arsenic Wastes from Pesticide Manufacturing and Usage

Industrial awareness for the hazardous properties of the arsenic compounds has an important influence upon the design of industrial processes for the manufacture of arsenic pesticide compounds. Batch processes are normally employed in the production of these materials. The modern plants that produce these materials can generally be characterized by their complete containment of any by-products or contaminated effluents that result from these processes. More often than not, the only liquid effluents from any of these processes are small amounts of contaminated water from equipment washout and these are held in evaporating ponds at the plant site.[1740] In the formulation of dry products, the water is driven off by means of steam-heated, continuous drum dryers or of spray drying apparatus. Scrubbing equipment treats the steam effluent from the drying equipment and the scrubbing liquids are recycled for use as makeup solutions for the next batch. Grinding and bagging of the products are performed in a closed area with devices to control the emission of particulates from the operation. Bag filters are in common use and particulates removed from the bags are packaged for sale. Because of the caution and control exercised in the production process, the only major sources of arsenic wastes from pesticide manufacture are: (1) arsenic contaminated filter cakes when purification of a liquid formulation is required; and (2) arsenic contaminated by-products.

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*Based on mass balance calculations and the following assumptions: (1) 1/3 of the phosphate rock is available phosphorus; (2) phosphate rock contains an average of 10 ppm arsenic; and (3) wet process acid contains 5 ppm arsenic.

†Rollins Environmental Services data.

Of the four major inorganic arsenic pesticides, no arsenic containing wastes have been identified in the manufacture of lead arsenate, calcium arsenate, or copper acetoarsenite. Sodium arsenite is always sold commercially as a liquid formulation and the liquid solution is usually filtered before drumming. The resulting filter cake is buried in public dumps. The quantity and composition of the waste filter cake generated are not known, but is believed to be of low volume and contain both sodium arsenite and arsenic trioxide, along with filter aid and water.

Among the organic arsenicals, solid wastes containing sodium chloride, sodium sulfate, and 1 to 1.5 percent cacodylate contaminants are generated in the cacoylic acid production process.[2215] The rate at which this waste material is produced is not known, but at the present time there are 60,000,000 lb being stored in concrete vaults in the Marinette, Wisconsin area. There are currently no plans for the waste material other than to store it indefinitely.[2214] Arsenic wastes from the manufacture of other organic arsenicals have not been identified.

Aerojet General Corporation manufactures arsenic fungicide products and still bottom residues are generated from the process.[1643] The waste amounts to about 16,000 lb, contains approximately 15 percent arsenic in various chemical forms, and is currently stored in 55-gal. drums at Sacramento, California.

The use of formulated pesticides packed in containers always results in some residue remaining in the containers. The arsenate pesticides are usually formulated as dusts, granules, or wettable powders and packed in sift proof, multiwall paper bags. The amount of pesticide residue left in these containers after emptying is relatively small. The arsenites and organic arsenicals, however, are normally formulated as liquid solutions. As such, there are usually 0.5 oz to 1 lb of liquid residue left in the empty containers, depending on the shapes and sizes of the containers. At the present time, arsenic pesticide usage is dominated by the three major organic arsenicals--cacodylic acid, and the mono- and di-solium salts of methane arsonic acid. The amount of these organic arsenicals left as residues in used pesticide containers is estimated to be about 35,000 lb (as active ingredient) per year. The geographical distribution of these pesticide residue wastes was calculated on the basis of the proportional regional usage of organic arsenicals on crops by farmers (Table 1). The assumptions and methods of computation employed in estimating the total quantity and geographical distribution of the pesticide residue wastes are described in detail in the report "Pesticide Wastes" elsewhere in this Volume.

Surplus Arsenic Pesticides and Arsenic Contaminated Soil

Surplus arsenic pesticides currently in storage awaiting disposal include the following[2222,2243]: (1) Department of Defense - 1,624 lb of 98 percent lead arsenate in Texas, 12 lb of 98 percent lead arsenate in Michigan, 110 gal. of sodium arsenite in Florida, 30 gal. of sodium arsenite in New York, 65 gal. of sodium arsenite in Illinois, 1,620 gal. of sodium arsenite in Alaska, and 30,000 lb of 5 percent copper acetoarsenite solution in Florida; (2) state/regional Environmental Protection Agency - 96 lb of 95 percent lead arsenate and 305 lb of 70 percent calcium arsenate in

Washington, and 2,460 units of arsenate containing Harris Ant Buttons in Georgia; and (3) pesticide manufactures - an estimated 24,000 lb of lead arsenate at South Gate, California.

The extensive use of arsenic pesticide in the past, particularly lead arsenate, has also led to soil sterilization and rendered large acreages of farm land unusable for the growth of future crops.[2271] In addition, the bottoms of evaporation ponds and lagoon systems for the treatment of waste water from arsenic pesticide manufacturers are often contaminated with arsenic in the form of arsenic trioxide. The lagoon system at Rocky Mountain Arsenal, for example, has been used over the years by pesticide manufacturers as well as the military for the discharge of their waste water, and its bottom mud now contains 10 to 100 ppm arsenic.

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WASTES OF CADMIUM AND CADMIUM COMPOUNDS

The principal sources of cadmium wastes have been identified as: (1) rinse water and dragout from the electroplating industry; (2) waste sludges from paint manufacture; (3) paint residue left in used paint containers; and (4) wash water from the manufacture of nickel-cadmium batteries.

Detailed discussions of the cadmium wastes from the electroplating industry and battery manufacture can be found elsewhere in this volume in the reports "Wastes from the Electroplating Industry" and "Wastes from the Manufacture of Batteries", respectively. Likewise, a more complete discussion of the cadmium wastes from paint manufacture and paint residue left in used paint containers as well as the assumptions used in the computation of the waste quantities can be found in the report "Toxic Paint Wastes". A brief summary for these is given below followed by a discussion of other sources.

The electroplating industry is the largest user of the cadmium metal and is at the present also the largest source of cadmium wastes. The cadmium wastes are generated primarily as the result of the rinsing operations, and the typical aqueous waste stream contains 100 to 500 ppm cadmium, along with other heavy metals, cyanides, and metal surface cleaning agents. Large volumes of liquid waste streams having a much higher cadmium content, however, have also been reported. An example of such a waste stream contains 1.5 percent cadmium cyanide, 8.5 percent sodium cyanide, 3 percent sodium hydroxide, and traces of other metals. The total amount of cadmium wastes (as cadmium) from the electroplating industry has been estimated to be 1.44 million lb per year. The geographical distribution of the electroplating wastes was calculated on the basis of the distribution of "value added by manufacture" dollar amounts for finished metal products in the United States (Table 1).

Cadmium wastes are generated in paint manufacture as a result of the kettle washings and equipment cleanup. The two most important cadmium pigments are the cadmium sulfide and the cadmium sulfoselenide. Cadmium in

TABLE 1

WASTES OF CADMIUM AND CADMIUM COMPOUNDS

Source and Material	Bureau of Census Regions I	II	III	IV	V	VI	VII	VIII	IX	Total
					Annual Waste Production (lb/year)					
Paint Sludge										
Cadmium	150	1,100	1,550	350	450	250	400	50	800	5,100
Sludge	0.92×10^6	8.12×10^6	11.32×10^6	2.40×10^6	3.16×10^6	1.76×10^6	2.74×10^6	0.44×10^6	5.97×10^6	36.83×10^6
Paint Residue										
Cadmium	2,100	6,500	7,000	2,600	5,400	2,200	3,400	1,400	4,700	35,300
Old paint	13×10^6	41×10^6	44×10^6	16×10^6	34×10^6	14×10^6	21×10^6	9×10^6	29×10^6	221×10^6
Cadmium from electroplating	1.88×10^5	4.10×10^5	4.64×10^5	0.65×10^5	0.70×10^5	0.33×10^5	0.52×10^5	0.10×10^5	1.48×10^5	14.40×10^5
Cadmium from battery manufacture	530	1,600	-	530	530	-	-	530	-	3,720
					Stored Wastes (lb)					
Cadmium oxide	-	-	-	-	-	-	-	200	-	200

these forms are found in the solvent-based waste paint sludges, which typically contain 27.5 percent pigments, 25.0 percent binders, and 47.5 percent organic solvents. It is estimated that 5,100 lb of cadmium are lost through 37 million lb of solvent-based paint sludges per year. The geographical distribution of these waste paint sludges was calculated on the basis of the regional distribution of "value added by manufacture" dollar amounts for paints and allied products (Table 1).

The paint residues left in used paint containers constitute another source of cadmium waste. It is estimated that as much as 35,300 lb of cadmium are lost through these paint residues each year. The geographical distribution of these paint residue wastes was calculated on the basis of the population distribution in the United States (Table 1).

The major source of cadmium waste in the manufacture of nickel-cadmium batteries (sintered-plate type) is the wash water that is used to remove excess material from the plates. The typical waste water effluent contains cadmium hydroxide, potassium hydroxide, and potassium nitrate, usually in fairly high concentrations since the deionized water often used is expensive and is applied in minimum quantities. Cadmium losses from battery manufacture amount to 3,720 lb per year. The geographical distribution of the cadmium losses from battery manufacture was calculated on the basis of the regional distribution of "value added by manufacture" dollar amounts for electrical supplies produced in the United States (Table 1).

Cadmium containing flue dusts are released to the atmosphere from the metallurgical processing of cadmium-bearing ores. Cadmium is often found as the sulfide greenockite dispersed in zinc sulfide ores, and also in lead ores, copper ores, and other ores that contain zinc minerals. As a result, the zinc metallurgical processing plants and the lead and copper smelters have been found to be the largest sources of cadmium emissions to the atmosphere, in spite of the fact that all these refineries are normally equipped with electrostatic precipitators and/or bag filters for dust collection. Most of the atmospheric emissions of cadmium occur during the roasting and sintering of zinc concentrates. The emissions are composed of cadmium and other metals, and the cadmium contained in the dusts emitted may be in the form of cadmium oxide, or combined with sulfur as cadmium sulfate. Based on material balance data obtained from processing companies, the total cadmium emissions from metallurgical processing has been estimated to be 2.1 million lb in 1968 by Davis.[1086] These cadmium containing flue dusts, however, are not to be considered as a solid waste problem. Cadmium containing flue dusts are currently being sent to cadmium recovery plants for processing, and in the event that more stringent air pollution standards were adopted, the additional quantity of cadmium dusts collected could be treated accordingly.

Under normal circumstances, there are only small quantities of surplus cadmium chemicals in storage awaiting disposal. At present, this includes only 100 lb of cadmium oxide flakes and 100 lb of cadmium oxide powder in Department of Defense facilities in New Mexico.

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WASTES OF LEAD COMPOUNDS

The principal sources of lead wastes of concern have been identified as: (1) waste sludges from petroleum refineries; (2) waste sludges from the manufacture of alkyl lead compounds; (3) waste solvent-based paint sludges from paint manufacture; (4) paint residue left in used paint containers; (5) waste sludges from the manufacture of lead acid batteries; and (6) solvent and water washes from printing ink production.

Detailed discussions of the lead wastes from paint manufacture and paint residue left in used paint containers as well as the assumptions used in the computation of the waste quantities can be found in the report "Toxic Paint Wastes" elsewhere in this volume. Likewise, a more complete discussion of the lead wastes from battery manufacture can be found in the report "Wastes from the Manufacture of Batteries". Included in later sections of this report are discussions on the lead wastes from petroleum refineries, alkyl lead manufacturers, and printing ink production.

The major lead containing pigments include white lead, red lead, leaded zinc oxide, chrome green, chrome yellow, chrome orange, and molybdate orange. Lead is present in these pigments as the oxide, the carbonate, the hydroxide, the chromate, and the molybdate. In paint manufacture, lead is found in the waste solvent-based paint sludges which typically contain 27.5 percent pigment, 25.0 percent binders, and 47.5 percent organic solvents. It is estimated that a total of 640,000 lb of lead are lost through 37 million lb of solvent-based paint sludges per year. The geographical distribution of these waste paint sludges was calculated on the basis of the regional distribution of "value added by manufacture" dollar amounts for paints and allied products (Table 1).

The paint residues left in used paint containers constitute another source of lead waste. It is estimated that 4.4 million lb of lead are lost through these paint residues each year. The geographical distribution of these paint residual wastes was calculated on the basis of the population distribution in the United States (Table 1).

TABLE 1.
WASTES OF LEAD COMPOUND

Source & Material	Bureau of Census Regions I	II	III	IV	V	VI	VII	VIII	IX	Total
	Annual Waste Production (lb/year)									
Petroleum refineries, waste lead sludge	-	1.16×10^6	1.72×10^6	0.66×10^6	0.05×10^6	0.14×10^6	4.19×10^6	0.39×10^6	1.35×10^6	9.66×10^6
Alkyl lead manufacture, waste lead sludge	-	1.0×10^5	-	-	-	-	3.2×10^5	-	1.0×10^5	5.2×10^5
Waste paint sludge										
Lead	16,000	140,000	196,000	42,000	55,000	30,000	47,000	8,000	103,000	637,000
Sludge	0.92×10^6	8.12×10^6	11.32×10^6	2.40×10^6	3.16×10^6	1.76×10^6	2.74×10^6	0.44×10^6	5.97×10^6	36.83×10^6
Paint residue										
Lead	2.58×10^5	8.13×10^5	8.81×10^5	3.28×10^5	6.69×10^5	2.77×10^5	4.22×10^5	1.81×10^5	5.81×10^5	4.41×10^6
Old paint	13×10^6	41×10^6	44×10^6	16×10^6	34×10^6	14×10^6	21×10^6	9×10^6	29×10^6	221×10^6
Battery manufacture as lead	2.56×10^5	4.70×10^5	2.29×10^5	0.46×10^5	0.70×10^5	0.08×10^5	0.25×10^5	0.15×10^5	2.21×10^5	13.40×10^5
Printing ink production, as lead	-	11,500	6,000	-	-	-	-	-	3,500	21,000

Lead wastes from the manufacture of lead acid batteries are generated as a result of the mixing operation of the lead acid pastes and the application of these pastes to support grids. It is estimated that over 1.3 million lb of lead, mostly as lead sulfate in neutralized sulfuric acid, are lost through the waste sludges from battery manufacture each year. The geographical distribution of the lead losses from battery manufacture was calculated on the basis of the regional distribution of "value added by manufacture" dollar amounts for electrical supplies produced in the United States (Table 1).

Lead Wastes from Petroleum Refineries

Tetraethyl lead is the major antiknock agent that is normally added to the finished product of gasoline in tank cars or storage tanks. After an extended period of time, sludges containing tetraethyl lead accumulate at the bottom of the storage tanks of the leaded gasoline. When it becomes necessary to take the storage tank out of service for repair or cleaning, the sludges are pumped out and become the major lead wastes from the petroleum refineries. The sludges typically contain a 1 percent mixture of tetraethyl lead and lead oxide, along with gasoline hydrocarbons, iron oxide, silt, and water.

On a survey of four major petroleum refineries in Contra Costa County, California, conducted by the Western Oil and Gas Association and the California Department of Public Health in 1967,[0469] the total tetraethyl lead wastes were found to amount to 270 tons per year. Based on the gasoline production rates, the tetraethyl lead wastes for the State of California and the United States were calculated to be 675 tons per year and 4,800 tons per year, respectively. Using the 1 percent figure as the typical tetraethyl lead concentration in the waste sludge, the net tetraethyl lead waste was determined to be 96,000 lb per year. The geographical distribution of the total waste was calculated on the basis of the gasoline production in each region as classified by the Bureau of Census (Table 1).

Lead Wastes from Alkyl Lead Manufacture

In addition to the petroleum refineries, organic lead sludges are also generated in manufacturing facilities where alkyl lead compounds are produced. These organic lead sludges are now being stored in holding basins at the manufacturing plants awaiting the development of technically and economically feasible lead recovery methods.

The organic lead waste sludges from alkyl lead manufacture contain an average of 0.5 to 1.0 percent tetraethyl and tetamethyl lead. The annual production of organic lead waste from an alkyl lead manufacturing plant at Antioch, California has been reported to be 50 tons per year.[1508] Assuming the same waste production factor at the other five alkyl lead manufacturing plants,* the total annual production of organic lead waste sludge was estimated to be 260 tons. These organic lead wastes were distributed geographically according to the locations and production capacities of the alkyl lead manufacturing plants in each Bureau of Census region (Table 1).

Lead Wastes from Printing Ink Production

In printing ink production, the majority of manufacturers have either phased out or curtailed the use of lead pigments in their products. There are, however, a number of manufacturers that still produce certain types of printing inks with lead pigments, and lead containing wastes are generated as a result of the operations to clean up the ball mills, mixing tanks, and other equipment. These liquid wastes typically contain 0.5 to 1.5 percent lead pigment mixed with varying amounts of other metals in organic solvents and water washes.[2618]

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* DuPont at Deepwater, New Jersey; Ethyl Corporation at Baton Rouge, Louisiana and Houston, Texas; Houston Chemical at Beaumont, Texas; Nalco Chemical at Houston, Texas.

Five leading printing ink manufacturers* currently account for about 85 percent of the total U.S. production.[2617] Information obtained from contacting these manufacturers and a waste disposal firm handling printing ink production wastes, the Pollution Control Corporation of America† (PCCA),[2617,2618,2619] showed that the lead containing wastes generated from each plant ranged from 250 to 10,000 gal. per month. The only definitive quantity information, however, was the figures supplied by PCCA indicating that 7,200 gal. of aqueous wastes containing an average of 1 percent lead were generated per month from a printing ink manufacturer with 30 million lb per year production capacity.[2618] On this basis, the waste generation factor was calculated to be 290 lb of lead per million pound of printing ink produced, and the corresponding total lead loss from the printing ink industry was estimated to be 21,000 lb per year. The geographical distribution of these lead wastes was computed according to the production capacity of the printing ink manufacturing facilities in each region of the United States as classified by the Bureau of Census (Table 1).

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* These five manufacturers are: (1) Tenneco Chemicals Inc., Cal Ink Division; (2) Inmont Corporation; (3) Sun Chemical Corporation; (4) Cities Service Company, Levey Division; and (5) Sinclair and Valentine Printing Inks.

† The Pollution Control Corporation of America has 13 plants across the United States to handle industrial wastes.

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WASTES OF SOLUBLE COPPER COMPOUNDS

The major sources of soluble copper wastes generated in the United States are the electroplating industry, the printed circuit industry, spent copper catalysts from the chemical industry, copper pickle liquors, and the textile industry. The soluble copper wastes are of particular concern because of their high degree of toxicity to aquatic organisms.

Copper wastes from the electroplating industry come from several sources, but the most important of these is the rinse water. A typical waste stream has soluble copper concentrations in the range 50 to 10,000 ppm, alkaline concentrations from 1 to 20 percent as sodium hydroxide, along with some cyanides, chromium, nickel, and lead. It is estimated that there are 2.1 million lb of copper lost in the waste streams from the electroplating industry each year. The geographical distribution of these wastes was calculated on the basis of the distribution of "value added by manufacture" dollar amounts for finished metal products in the United States (Table 1). A more complete discussion of the copper wastes from the electroplating industry can be found in the report "Wastes from the Electroplating Industry".

Copper wastes from the printed circuit industry are generated mainly in the etching process where the copper not comprising the circuit is chemically removed from the circuit board. It is estimated that 456,000 lb of copper wastes (as copper) are generated each year in this industry.

The chemical industry generates a significant quantity of copper wastes each year by discarding spent copper catalysts. Based on the information supplied by industry sources, 600,000 lb of copper wastes (as copper) are generated annually from spent copper catalysts.

TABLE 1

COPPER WASTES (AS COPPER) GENERATED BY U.S. INDUSTRY

	Bureau of Census Regions									
Sources	I	II	III	IV	V	VI	VII	VIII	IX	Total
					Annual Waste Production (lb/yr)					
Electroplating	2.75×10^6	5.99×10^5	6.78×10^5	0.95×10^5	1.03×10^5	0.48×10^5	0.76×10^5	0.15×10^5	2.17×10^5	21.06×10^5
Printed Circuit	8.71×10^4	16.05×10^4	7.80×10^4	1.55×10^5	2.38×10^4	0.26×10^4	0.86×10^4	0.49×10^4	7.51×10^4	45.61×10^4
Spent Copper Catalysts	2.22×10^4	15.75×10^4	13.66×10^4	2.90×10^4	9.56×10^4	5.74×10^4	7.71×10^4	1.55×10^4	0.91×10^4	60.00×10^4
Pickling of Copper	15.00×10^5	14.77×10^5	23.92×10^5	4.03×10^5	8.58×10^5	6.63×10^5	2.54×10^5	2.74×10^5	5.79×10^5	84.00×10^5
Textile Industry	6.35×10^5	8.52×10^5	1.16×10^5	-	39.12×10^5	2.22×10^5	0.87×10^5	-	1.76×10^5	60.00×10^5

Copper wastes are generated from the acid pickling of copper largely as a result of dragout of liquor from the pickling vats and the dumping of the vats when the acid strength is depleted. It is estimated that copper wastes (in the form of a liquid) from the pickling of copper amount to 8,400,000 lb of copper annually.

Copper wastes from the textile industry are generated in the dyeing and finishing of cotton yarns. It is estimated that copper wastes (in the form of a liquid) from the textile industry amount to 5,975,000 lb of copper annually.

Detailed discussions of the general assumptions used in the computation of the quantities information and the forms and composition of the waste streams from the printed circuit industry, spent copper catalysts, pickling of copper, and the textile industry are included in the following sections of this report.

Copper Wastes From the Printed Circuit Industry

Approximately 15,000,000 lb of copper foil were produced in 1971 for use in the printed circuit industry. Since 5 percent of this is exported, approximately 14,250,000 lb of copper foil is supplied to five major laminators in the United States who apply the copper to laminated circuit boards. The boards, with the layer of copper affixed, are then sent to the printed circuit plants. At these plants, the board is etched and becomes the finished printed circuit.[2601,2607]

Copper wastes from circuitry manufacture are generated largely as a result of the etching process in which the excess copper is removed from the circuit board. After the board has been etched, the remaining copper (which comprises the circuit) is sometimes electroplated with a finishing coat of copper. There is some copper loss in the electroplating operation, but it is small compared to the loss of copper in the etching process.[2607]

The composition of the concentrated liquid waste generated in the etching process is dependent upon the type of etchant used and the type of acid solution used for cleaning. Ferric chloride is the major etchant material, but cuprous chloride, ammoniacal chlorite, ammonium persulphate, and chrome/sulfuric solutions are also used. The acids used for cleaning are hydrochloric, fluoroboric, concentrated sulfuric, acetic and citric acids.

The waste is generally characterized by a high concentration (1,000 to 50,000 ppm) of soluble copper. A typical waste may contain ferric chloride solutions having soluble copper contents of 3,000 to 50,000 ppm, lead and nickel in the range of 10 to 50 ppm, and hydrochloric acid concentrations of 15 to 30 percent.*

The plant manager of a major printed circuit plant in the Los Angeles area (Cinch Graphic) supplied a waste generation factor of 3.2 percent for the printed circuit industry and indicated that this is a representative factor within the industry.[2607] Since 14.25 million lb of copper foil is used by the printed circuit industry each year, 3.2 percent of this figure gives 456,000 lb of water soluble copper waste (as copper) generated per year by this industry.

The 456,000 lb of copper waste were distributed geographically on the basis of the distribution of "value added by manufacture" dollar amounts for electrical supplies produced in the United States and by Bureau of Census regions (Table 1).

Copper Wastes from Spent Copper Catalysts

It is estimated that there are over 300 tons of copper waste (as copper) generated annually by the chemical industry from spent catalysts.[2606] This figure was supplied by industrial contacts that are in the business of buying spent catalysts and reselling it to other companies that recover the metal content.[2606] Industry sources indicated that the 300 ton per year figure is probably conservative.[2606]

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*Rollins Environmental Services data.

It is impossible to relate the amount of copper waste to the quantity of copper used in the production of copper catalysts each year. This is due to the fact that many producers of copper catalysts enter into secrecy agreements with both suppliers of copper and the companies that they supply.[2606]

The composition of the sludge that comprises the spent copper catalyst depends upon the type of copper catalyst used and the particular segment of the chemical industry utilizing it. A typical waste may contain 27 percent cuprous-cupric chloride tar in 65 percent mixed organics (from the production of aniline).*

The geographical distribution of the 600,000 lb of copper waste was computed on the basis of the distribution of "value added by manufacturer" dollar amounts for the chemical industry and by Bureau of Census regions (Table 1).

Copper Wastes From the Pickling of Copper

The treatment of copper in an acid bath, known as pickling, removes oxide from the metal surface and produces a bright sheet stripped down to bare metal and suitable for finishing operations. Both sulfuric and hydrochloric acid are used in the industry. Regardless of which acid is used, the disposal of spent pickle liquor is a serious problem which has still not been satisfactorily solved for the metal finishing industry at reasonable cost.[0285]

Pickling may be done either batchwise or as a continuous operation. Usually the acid is prepared at about 5 to 15 percent strength, depending on the work to be processed in the pickle tank and the type of acid used for pickling. As the acid works on the oxide surface, there is a gradual buildup of copper compounds (largely copper sulfate when sulfuric acid is used) in the pickle bath and a depletion of the free acid strength. When the copper content reaches a level which begins to slow the pickling operation, the bath is either dumped or reprocessed. In some pickling operations the acid is continually withdrawn for disposal or reprocessing in order to maintain uniform pickling conditions for all the copper passing through the operation.

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*Rollins Environmental Services data.

The copper leaving the pickle vat will drag out some of the liquor with it and carry this liquor into the subsequent rinsing and neutralizing operation. The loss of the spent pickle liquor (spent liquor plus acid mixture) by dragout varies, but it can run as high as 20 percent of the acid used.[0285]

In some cases the dragout of liquor from the pickling vat may be so great that the copper contamination level in the pickle vat never reaches an objectionable level. The strength of the vat is then controlled entirely by makeup of fresh acid and water to bring the acid to its proper dilution.

The discharge from the pickling area generally includes spent strong pickle liquor and acidic rinse water which must be neutralized before it can be discharged.

A typical spent pickle liquor may contain 0.5 percent copper sulfate with 0.2 percent stannous sulfate in 4 percent sulfuric acid with traces of sodium phosphate-borax.*

A consultant specializing in the treatment of copper pickling liquor wastes (of Lancy Laboratories) stated that between 0.1 and 0.2 percent of the copper is lost during the pickling operation.[2611] An average loss factor of 0.15 percent was used to estimate the total amount of copper waste generated from the pickling of copper in the United States. Since 5.6×10^9 lb of copper metal (including new refined and secondary copper) is processed in the United States each year, 0.15 percent of this figure gives 8,400,000 lb of copper waste generated from the pickling of copper annually. In this calculation, it was assumed that all of the copper used in the United States is eventually pickled.

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*Rollins Environmental Services data.

Industry sources also indicated that a large pickling mill may lose up to 800 lb of copper per day through dragout and rinsing operations.[2611] Since there are about ten large pickling mills in the United States, the loss from the mills alone accounts for 2,400,000 lb per year of the copper waste from pickling. The other 6,000,000 lb per year of copper waste can easily be accounted for by the countless small shops in the country that pickle copper.

The 8,400,000 lb of copper wastes were distributed geographically on the basis of the distribution of "value added by manufacture" dollar amounts for the nonferrous metal rolling and drawing industry in the United States and by the Bureau of Census regions (Table 1).

Copper Wastes from the Textile Industry

Copper wastes from the textile industry are generated mainly in the dyeing and finishing of cotton cloth.

There are varied methods of dyeing cotton and many types of dyes are used. Small volumes of cloth are dyed on jigs--which are small, tapered tanks with the large surface area at the top. Larger volumes of cloth are usually dyed in a continuous dyeing range, which consists of a number of boxes through which the cloth passes to be dyed, oxidized, dried and finished. Two of the most important dyes are direct dyes and aniline black dyes.

Direct dyes (water soluble) are applied with or without heat directly to cotton with salt (10 to 60 percent) and sodium carbonate (1 to 5 percent). Some chemicals, such as copper sulfate (others are acetic acid and formaldehyde) may be used occasionally to modify the shade or fastness.[0085]

Aniline black dye is an insoluble pigment produced by the oxidation of aniline. The cloth is passed through a dye bath typically consisting of 90 lb of aniline hydrochloride, 35 lb of sodium chlorate, and 13 lb of copper sulphate in 100 gal. of water. After impregnation, the cloth is passed over stream-heated rollers to develop the black pigment. Soaping and washing complete the operation. Since the dye bath is costly, it is seldom dumped.

It is important to note that dye wastes are extremely variable in contaminating matter. It is common, in aniline dyeing, to discharge 15,000 to 23,000 gal. of waste per 1,000 lb of cotton processed. In direct dyeing there are 1,700 to 6,400 gal. of waste per 1,000 lb of cotton processed.[1185] All of the contaminants in dye waste come from the chemicals added to the dye baths.

The finishing operation imparts a smooth appearance and certain rigidity to the cloth. The cotton is often waterproofed, fire-proofed, or mildew-proofed. Copper wastes may be generated in the mildew proofing operation where copper ammonium fluoride and copper ammonium carbonate are the chemical agents used.[1662]

A typical dye waste from the textile industry may contain 900 ppm copper and 100 ppm chromium in a neutral aqueous mixture with coal tar dyes containing 400 ppm phenols (97% water).*

It is estimated that the textile industry generates 6,000,000 lb of copper wastes (as copper) annually. This number was obtained from the Booz-Allen data and confirmed by industry sources to be in the right order of magnitude. This is not an unreasonable amount of copper waste in light of the fact that the textile industry had a wastewater effluent of 128 billion gallons in 1971.[1185]

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*Rollins Environmental Services data

The 6,000,000 lb of copper wastes were distributed geographically on the basis of the distribution of "value added by manufacturer" dollar amounts for cotton finishing plants in the United States and by Bureau of Census Regions (Table 1).

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WASTES OF SELENIUM AND SELENIUM COMPOUNDS

Selenium is not found in significant quantities as wastes. The only major source of selenium waste that has been identified is in the manufacture and reconditioning of xerox drums (Table 1), and this is discussed in the following section of this report.

Selenium is combined with cadmium and sulfur as cadmium sulfoselenide and used in cadmium red and cadmium orange pigments. The ratio of cadmium to selenium in a typical light red shade is 5 to 1, while in a maroon red shade it is 3 to 1. Cadmium orange is normally a mixture of the cadmium red and cadmium yellow pigments. About 51,000 lb of selenium are used in these cadmium pigments each year. Because of the relatively low volume usage of selenium in paints and allied products, only an estimated 370 lb of selenium are lost in the waste solvent-based paint sludges from paint manufacture each year, and an additional 2,600 lb as paint residue left in used paint containers (Table 1). A more complete discussion of the selenium paint wastes can be found in the report "Toxic Paint Wastes".

Selenium Wastes from the Manufacture of Duplicating Machines

Amorphous selenium, a super-cooled state of liquid selenium, has found extensive use as a coating on metal cylinders in the field of xerography where low electrical conductivity is essential. The low conductivity of selenium permits the development step to be carried out before the electrostatic image is destroyed by electrical conduction through the plate.

The manufacture of selenium plates and drums is generally of a single basic design. The substrate is made of meticulously cleaned, oxidized aluminum in sheet or drum form, onto which high purity amorphous selenium is vacuum plated. About 4 lb of selenium are required per 100 square ft

TABLE 1

WASTES OF SELENIUM AND SELENIUM COMPOUNDS

	Bureau of Census Regions									
Source and Material	I	II	III	IV	V	VI	VII	VIII	IX	Total
	Annual Waste Production (lb/year)									
Waste Paint Sludge										
Selenium	10	80	115	25	30	20	25	5	60	370
Sludge	0.92×10^6	8.12×10^6	11.32×10^6	2.40×10^6	3.16×10^6	1.76×10^6	2.74×10^6	0.44×10^6	5.97×10^6	36.83×10^6
Paint Residue										
Selenium	150	470	510	190	390	160	240	110	340	2,560
Old Paint	13×10^6	41×10^6	44×10^6	16×10^6	34×10^6	14×10^6	21×10^6	9×10^6	29×10^6	221×10^6
Xerox Drum Manufacture										
Selenium	-	450	-	-	-	-	-	-	-	450
Solid waste	-	7×10^5	-	-	-	-	-	-	-	7×10^5
Acid waste	-	5×10^4	-	-	-	-	-	-	-	5×10^4

of cylinder surface, and approximately 158 tons of selenium were used in xerography in 1969.[2309] Xerox drums normally contain selenium coatings 0.002 in. thick.

In addition to selenium, arsenic is used as an alloying element to control color sensitivity and selenium crystallization in xerographic photoreceptors. The use of arsenic varies from 5,000 to 20,000 lb per year, depending on the type of alloy produced and the production levels required.[2674] Projected purchase of arsenic in 1973 is about 13,000 lb.[2674]

Replacement of the selenium coating on xerox drums may be necessary after reproducing 30,000 to 500,000 copies.[2309] The usual practice is to remove the worn out cylinder from the copying machine and return it to the factory for reconditioning. During the reconditioning process, coatings from the spent xerox drums are removed through heat stripping and mechanical chipping (lathe) operations, and the selenium and arsenic are reclaimed from the alloy chips through further reprocessing.[2674] The records at Xerox showed that for the past three years (1970 to 1972), 93 percent of all the xerox drums coated at the Joseph C. Wilson Center for Technology in Webster, New York* were shipped to the United States or Canada and 90 percent were returned for reclamation and recycle.[2674] Overseas shipments from the Wilson Center, however, are not normally returned.

Detailed information on the types, quantities, forms and composition of the selenium and arsenic-bearing wastes generated during the manufacture and reconditioning of xerox drums was provided by the Xerox Corporation (Table 2).[2674] This information indicated that about 700,000 lb of solid wastes containing 300 to 400 lb of arsenic and selenium are generated each year, principally from the following sources: (1) polishing of previously stripped aluminum xerox drums; (2) air and water filtration systems from alloying arsenic in selenium; and (3) coating room laminar flow filters, shipping containers for arsenic and selenium, and toner residues from xerographic developer reclaim. Of the selenium and arsenic found in

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*The selenium and arsenic coated drums are manufactured and reconditioned exclusively at Xerox's Webster, New York facility.

TABLE 2.
ARSENIC AND SELENIUM WASTES FROM THE MANUFACTURE OF XEROX DRUMS

Waste	Se Conc., ppm	As Conc. ppm	Major Component	Minor Component	Physical Characteristics	Annual Volume lb.
Dry buffing wastes	160	40	Cotton	Aluminum, fatty acid	Fine fibers	240,000
Rotoclone sludge	200	50	Cotton	Aluminum, fatty acid	Fine fibers in water	220,000
Spent buffing wheels	150	50	Steel (55%)	Cotton	Cotton cloth on steel drum 40 lb each	200,000
Caustic mask*	1,800	1,200	Caustic soda solution	--	Liquid and sludge	50,000
Developer reclaim	300	60	Toner		Powder	20,000
Vacuum pump oil filters	6,000	20	Organic fiber	Mineral oil	Large pieces	1,800
Selenium bags	200	0	Polyethylene	--	Film	300
Arsenic bottles	0	500	Polyethylene	--	Quart bottles	1,000
Hi-Flo filters	90,000-100,000		Glass fiber	--	Fiber blanket with metal frame	100
Coating room filters	150,000	50,000	Glass fiber	Steel,tricresylphosphate	Typical home furnace filter	1,000
Hi-Cap filter	90,000-100,000		Polymer fiber	Steel	Large, low density	100
Absolute filter	4,000	2,000	Paper fiber & aluminum foil laminate	--	Paper and aluminum foil	200
Demineralizer resin	4,000	30,000	Resin	--	Granules	700

*Liquid waste

TABLE 2. (CONTINUED)
ARSENIC AND SELENIUM WASTES FROM
THE MANUFACTURE OF XEROX DRUMS

Waste	Se Conc., ppm	As Conc., ppm	Major Component	Minor Component	Physical Characteristics	Annual Volume lb.
Shotter water filters	3,000	2,000	Polymer fiber	--	Large pieces	400
Heat strip oven filters	20,000	--	Polymer fiber	--	Large pieces	600
Nitric acid cleaner*	11,000	6,000	Acid solution	--	Liquid	800
Sand--As/Se mixture	50,000	250	Sand	--	Coarse powder	1,000
Degreaser filters	450	50	Organic wool fibers	Trichlorethylene	Large units	2,000
Post-coat buff dry waste dust	150	100	Cotton	Cr^{+++}	Fibrous powder	500
Post-coat buff filter bags	500	300	Cotton	Cr^{+++}	Cloth	150
Post-coat buff degreaser filters	100	60	Organic fiber	Cr^{+++}	Large pieces	2,000

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*Liquid waste

the solid wastes, there is usually more selenium present than arsenic (Table 2), and approximately 25 percent of the selenium is combined with arsenic chemically, (e.g., arsenic triselenide), with the remaining selenium containing less than 1 percent arsenic in them.[2667]

Some liquid wastes are also generated through chemical solution operations for the removal of arsenic and selenium alloys from production hardware and tools. The total liquid waste amounts to 50,000 lb or 100 barrels a year, consisting primarily of caustic solutions.[2674] The arsenic and selenium components in these wastes are for the most part complex anions that are not identified at this time.

Because of the air pollution control systems (absolute filters, oil traps, etc.) installed at the manufacturing facility, only small quantities of arsenic and selenium are discharged to the atmosphere. The total discharged has been reported to be less than 20 lb of arsenic and selenium per year.[2674]

All of the arsenic and selenium-bearing solid and liquid wastes from Xerox are presently being shipped to the Nuclear Engineering Company in Sheffield, Illinois for disposal.[2674]

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WASTES OF BORON HYDRIDES

The boron hydrides (boranes) are compounds of boron and hydrogen. Of the various borane compounds, only diborane, pentaborane, and decaborane are of any commercial significance. There is currently one producer of boranes in the United States, the Callery Chemical Company, Callery, Pennsylvania,[2020] and diborane and decaborane are the only boranes manufactured at present.

Diborane Wastes

There is essentially no toxic waste generated in the production of diborane. The annual production of diborane was estimated at less than 200 lb, which is used almost exclusively for defect doping in the manufacture of semiconductors. Three major gas suppliers, Air Products and Chemicals Inc., the Linde Division, Union Carbide Corporation, and Matheson Gas Products, buy 10 mole percent diborane mixed with either argon, nitrogen, or hydrogen, and further dilute it to diborane concentrations from 10 ppm to 1,000 ppm (but most typically 100 ppm), and resell it to the semiconductor manufacturers. In the gas dilution process, diborane wastes are generated in the form of residual gas remaining in the manifolds after mixing is complete.

Air Products and Chemicals Inc. mixes diborane with H_2, N_2 or argon in three locations in the United States - Emmaus, Pennsylvania,[2017] Long Beach, California,[2015] and Houston, Texas. The Emmaus, Pennsylvania facility runs about 0.1 ft^3 every six months to a storage cylinder, which has been filling for six years and is currently half full. The Long Beach, California facility handles approximately 10 lb/yr of the 10 mole percent mixture. They occasionally vent "a few cc of the mixture" to the atmosphere with no monitoring or control. The Houston facility operates similarly to the Long Beach facility.

The Linde Division of the Union Carbide Corporation mixes diborane in five locations - East Chicago, Indiana; Houston, Texas; Keaseby, New Jersey; Linden, New Jersey; and Torrance, California.[2018] The Torrance, California

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facility uses approximately 60 lb/yr of the 10 mole percent mixture. After dilution there are usually a residue of 500 cc.

Matheson Gas Products mixes diborane in three locations - Cucamonga, California,[2011] Newark, California,[2010] and East Rutherford, New Jersey. The quantity of residual gas waste generated from these operations is not known.

Based on the information obtained, the quantity of diborane waste generated is less than 0.2 cu ft per plant each year. Since the residual gas wastes normally have a diborane concentration of 100 ppm, the diborane contained in these wastes is less than 1.54×10^{-6} lb per plant each year. These diborane wastes are distributed geographically according to the locations of the gas mixing facilities (Table 1).

Pentaborane Wastes

Pentaborane has been used for research in rocket fuels but is no longer being manufactured. There is, however, a stockpile of approximately 200,000 lb of pentaborane in storage at Edwards Air Force Base, California, in the Mojave Desert. Current consumption of pentaborane in the manufacture of the high temperature elastomer, Pentasil, amounts to only 50 to 75 lb per year, and no pentaborane containing waste is generated in this application.

Decaborane Wastes

The only decaborane waste identified is the several lb of toxic solid wastes generated each year in its production process. Aside from a small amount of decaborane used in classified research in solid propellants, 40 to 70 lb per year are used by the Olin Corporation, New Haven, Connecticut, in the manufacture of Dexsil, a patented high temperature elastomer.[2008] The high value of decaborane, however, causes Olin to recycle all decaborane containing streams in the manufacture of Dexsil, and no decaborane waste is released to the environment.

TABLE 1

WASTES OF BORON HYDRIDES

	Bureau of Census Regions									
Material	I	II	III	IV	V	VI	VII	VIII	IX	Total
					Annual Waste Production (lb/year)					
Diborane	-	6.0×10^{-6}	1.5×10^{-6}	-	-	-	3.0×10^{-6}	-	6.0×10^{-6}	16.5×10^{-6}
Decaborane	-	<10	-	-	-	-	-	-	-	<10
					Stored Waste (lb)					
Pentaborane	-	-	-	-	-	-	-	-	2×10^{5}	2×10^{5}

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WASTES OF CHROMIUM COMPOUNDS

The principal sources of chromium wastes in solid, semi-solid, or concentrated liquid form have been identified as: (1) dragout and rinse water from the metal finishing industry; (2) filter residue from sodium dichromate manufacture; (3) waste sludges from paint manufacture; (4) paint residue left in used paint containers; and (5) surplus chemicals under the custody of Department of Defense. In addition, significant amounts of chromium compounds in highly diluted forms (ppm level) are also lost through the waste waters from the textile industry, the leather tanning industry, and from the blowdown of cooling towers.

The chromium wastes from the metal finishing industry, the sodium dichromate manufacture, the textile industry, the leather tanning industry, and the blowdown of cooling towers are discussed in detail in individual sections of this report. Also included in later sections are brief discussions of the ammonium dichromate wastes from photo-engraving and potassium chromate and dichromate wastes.

The major chromium containing pigments include chrome green, chrome oxide green, chrome yellow, chrome orange, zinc yellow, and molybdate orange. With the exception of chrome oxide green (Cr_2O_3), all the other chromium pigments contain chromium in the hexavalent state and are normally only used in solvent-based paints. Chromium wastes are generated from paint manufacture in the form of waste paint sludges as a result of kettle washings and equipment cleanup. The typical solvent-based waste paint sludge is characterized by the following composition: 27.5 percent pigments, 25.0 percent binders, and 47.5 percent organic solvents. The typical water-based waste paint sludge, however, contains 15 percent pigments, 20 percent binders, and 65 percent water. It is estimated that a total of 140,000 lb of chromium are lost through 37 million lb of solvent-based waste paint sludges each year; and a total of 10,000 lb of chromium lost through 26 million lb of water-based waste paint sludges each year. The geographical distribution of these paint manufacturing wastes are calculated on the basis of the regional distribution of "value added by manufacture" dollars amounts for paints and allied products in the United States (Table 1). A more complete discussion of the sources and constituents of the chromium wastes from paint manufacture and the assumptions used in the computation of the total quantity of the wastes generated can be found in the report, "Toxic Paint Wastes."

The paint residues left in used paint containers discarded in municipal dumps constitute another source of chromium paint waste. It is estimated that approximately 1 million lb of chromium are lost through these paint residues each year. The geographical distribution of the paint residue wastes was calculated on the basis of the population distribution in the United States (Table 1). Again, a more complete discussion of the paint residue wastes can be found in the report "Toxic Paint Wastes".

Chromium compounds under the custody of Department of Defense and awaiting disposal include 34,243 lb of anhydrous sodium chromate, 3,040 lb of potassium dichromate, 2,030 lb of chromium trioxide, and smaller quantities of potassium chromate and sodium dichromate dihydrate distributed throughout the United States (Table 1). All these surplus chromium compounds were probably originally acquired for metal treatment and plating purposes.

Chromium Wastes from the Metal Finishing Industry

In the metal finishing industry, hexavalent chromium compounds are formulated for use as cleaning agents, oxidizing agents, surface preparation agents as well as the chemicals used to electroplate the decorative chrome surface. The wastes are generated from the extensive washing of the metal parts as well as spills, tank leakages, etc. Many of these metal treatment tanks became exhausted and have to be periodically drained.

TABLE 1
WASTES OF CHROMIUM COMPOUNDS

Source & Material	I	II	III	IV	V	VI	VII	VIII	IX	Total
					Annual Waste Production (lb/year)					
Chromium Waste from Metal Finishing as $Na_2Cr_2O_7$	7.99×10^6	17.41×10^6	19.70×10^6	2.76×10^6	2.99×10^6	1.39×10^6	2.21×10^6	0.44×10^6	6.31×10^6	61.20×10^6
Chromium Waste from Sodium Dichromate Production as Cr_2O_3	-	2.0×10^6	-	-	11.0×10^6	-	5.0×10^6	-	-	18.0×10^6
Solvent-Based Paint Sludge										
Chromium	3,000	30,000	42,000	9,000	12,000	7,000	10,000	2,000	22,000	137,000
Sludge	0.92×10^6	8.12×10^6	11.32×10^6	2.40×10^6	3.16×10^6	1.76×10^6	2.74×10^6	0.44×10^6	5.97×10^6	36.83×10^6
Water-Based Paint Sludge										
Chromium	240	2,160	3,010	640	840	470	730	120	1,590	9,800
Sludge	0.65×10^6	5.74×10^6	7.99×10^6	1.70×10^6	2.23×10^6	1.24×10^6	1.93×10^6	0.31×10^6	4.21×10^6	26.00×10^6
Paint Residue										
Chromium	0.56×10^5	1.78×10^5	1.92×10^5	0.72×10^5	1.46×10^5	0.61×10^5	0.92×10^5	0.40×10^5	1.27×10^5	9.63×10^5
Old Paint	13×10^6	41×10^6	44×10^6	16×10^6	34×10^6	14×10^6	21×10^6	9×10^6	29×10^6	221×10^6
Chromium Waste from Dyeing of Wool as $Na_2Cr_2O_7$	2.89×10^5	1.08×10^5	0.15×10^5	-	2.96×10^5	0.37×10^5	-	-	0.15×10^5	7.60×10^5

TABLE 1 - CONTINUED
WASTE OF CHROMIUM COMPOUNDS

Source & Material	Bureau of Census Regions									
	I	II	III	IV	V	VI	VII	VIII	IX	Total
	Annual Waste Production (lb/year)									
Chromium Waste from Leather Tanning as Cr	4.85×10^6	3.30×10^6	5.29×10^6	0.32×10^6	1.20×10^6	0.63×10^6	0.06×10^6	-	0.35×10^6	16.0×10^5
Chromium Waste from Cooling Tower Blowdown as $Na_2Cr_2O_7$	0.93×10^6	2.94×10^6	3.18×10^6	1.19×10^6	5.38×10^6	2.23×10^6	3.39×10^6	0.66×10^6	2.10×10^6	22.0×10^6
Chromium Waste from Photo-Engaving as $(NH_4)_2CrO_4$	230	740	790	320	590	250	380	160	520	4,000
Total Potassium Chromate/Dichromate Waste as $K_2Cr_2O_7$	2.76×10^5	6.14×10^5	6.87×10^5	1.19×10^5	2.60×10^5	1.10×10^5	1.68×10^5	0.33×10^5	2.53×10^5	25.20×10^5
	Stored Waste (lb)									
CrO_3	-	-	-	-	1,010	-	-	800	220	2,030
Na_2CrO_4	-	-	-	-	300	-	-	-	33,943	34,243
$K_2Cr_2O_7$	-	-	-	-	40	3,000	-	-	-	3,040
$Na_2Cr_2O_72H_2O$	-	-	-	-	520	-	-	-	-	520
K_2CrO_4	-	-	-	-	120	-	-	-	20	140

The composition of the chromium wastes from the metal finishing industry varies widely with the type of metals being processed, the metals being plated, the design of the equipment, and other important factors. The levels of chromium normally vary from a few ppm to a few percent of the total waste stream. Wastes from metal finishing may include many other metals such as copper, zinc, cadmium, and nickel. Likely to be included in the stream are grease, oils, acids, organic additives and cleaning agents. Information on the forms and composition of typical chromium containing metal finishing waste streams from various industry sources has been provided by Rollins Environmental Services and is summarized here (Table 2).

Discussion with various experts in the metal finishing industry has resulted in the conclusion that only 15 percent of all chromium compounds used in metal finishing ever end up as part of the finished product.[1471, 1472] The sodium dichromate consumption for metal treatment and plating amounts to 72 million lb per year, and the 85 percent of the chromium compounds discharged by the metal finishing industry amounts to 62 million lb per year when calculated as sodium dichromate.[1506] The geographical distribution of these chromium wastes was calculated on the basis of the regional distribution of "value added by manufacture" dollar amounts for the metal finishing industry in the United States and by Bureau of Census regions (Table 3).

Chromium Waste from Sodium Dichromate Manufacture

The chromite or chrome-ironstone ore is the raw material for sodium dichromate manufacture and contains principally ferrous chromite, ($FeO \cdot Cr_2O_3$), plus small amounts of aluminum, silicon, and magnesium oxides. In sodium dichromate manufacture, sodium chromate is first obtained by calcining a mixture of chromite ore, limestone, and soda ash, and is then reacted with sulfuric acid to yield the dichromate.[1501]

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* The chromium wastes occur in forms other than the dichromate, including trivalent chromium salts, chromic acid, and chromates (Table 2).

TABLE 2
TYPICAL METAL FINISHING WASTE STREAMS CONTAINING CHROMIUM

Waste Description	Form	Source: Industry/Process
3000 ppm of a mixture of chromium, 20% aluminum sulfate and 35% sulfuric acid (trace of copper, nickel, lead)	Liquid	Aluminum anodizing bath with drag out
12.5% chromic acid - dichromate in 10% to 30% sulfuric acid with 5000 to 120,000 ppm chromium (85% as Cr^{+3}) with 100-1000 ppm lead, copper and iron	Liquid	Metal finishing
Dilute chromic acid solution containing chromium +3 at 100-200 ppm and chromium +6 at 2000 to 4000 ppm with traces of organics (combined wash waters).	Liquid	Metal plating
Partially neutralized aqueous plating waste containing 5-10% zinc chromate, and 5-10% zinc phosphate contaminated with various organic oils.	Liquid	Zinc plating
Solutions of chromates and dichromates in sulfuric acid (6-12%) containing 5000-170,000 ppm chromium with copper, lead and traces of organics.	Liquid	Formation of protective and decorative coatings (metals)
0.1-0.5% chromium, 100-400 ppm copper, 100-600 ppm nickel in 5-10% aqueous hydrofluoric-hydrochloric acid.	Liquid	Plating preparation (metal)
1 to 20% chromium in solids concentrations of 10-80% from settling and/or dewatering processes. Includes copper in varying amounts with varying amounts of inert filter aids.	Sludge	Chemical process (plating operations, manufacturing, metallurgical)
100-1000 ppm chromium as alkaline cyanide solutions (6-20%) with copper in varying amounts with possible traces of organics, nickel, lead and zinc.	Liquid	Metal plating (formation of protective and decorative coatings)
5-6% chromic acid in water solution with 1% iron	Liquid	(1) Metal Plating (2) Shipbuilding
9% chromic acid in 13% aqueous sulfuric acid	Liquid	Metal finishing and plating
0.1-1% sodium or potassium dichromate in water, usually sulfuric acid present in a 1-15% concentration	Liquid	(1) Metal Finishing (2) Shipbuilding (3) Plating

The production process involves initially grounding the chromite ore to a fine powder (150 to 200 mesh) in ball mills, followed by blending of the raw material with soda ash, limestone and sufficient filter residue (from further along in the process) in a rotary mixer, and calcination of the mixture at high temperatures 2,000 F in a rotary kiln. After a 4-hr retention time, the roast from the kiln is sent directly to leaching tanks or thickeners, where the soluble chromate is dissolved in hot water and concentrated. The underflow from the last tray in the thickener is filtered, and the leached residue is dried in rotary dryers. A portion of the filter residue is recycled to the kiln feed where it serves to keep the reacting mass in a relatively dry condition, but the rest has to be disposed of as wastes.* The waste from this filtration process is in the form of a gangue residue, and contains approximately 4 percent trivalent chromium as Cr_2O_3 (dry weight basis), along with various amounts of iron, aluminum, calcium, and magnesium salts.[2591]

The chrome ore processing industry is represented by some rather old plants as well as a large new facility. The waste quantity information received covers one plant of older technology, and one plant which recently came on-stream.[2591,2673] This information provided a chromium waste generation factor of 34 lb Cr_2O_3 per ton or sodium dichromate product for the new plant, and a waste generation factor of 210 lb Cr_2O_3 per ton of product for the old plant. Based on the production capacity of the sodium dichromate plants[1501] and using the higher waste generation factor for the other old plants, it was estimated that a total of approximately 18 million lb of waste chromium, as Cr_2O_3, are generated each year from ore processing. This represents an estimated average waste generation factor of 130 lb Cr_2O_3 per ton of sodium dichromate product, a value that is in sharp disagreement with Booz-Allen's estimate of 1 lb Cr waste per ton of product. The raw material requirement for the production of sodium dichromate, as given by Faith et al,[1501] is 1.1 lb chromite ore (50% Cr_2O_3) per lb of sodium dichromate dihydrate produced. Mass balance calculations showed that this is equivalent to a waste generation factor of 90 lb Cr_2O_3 per ton of sodium dichromate product, thus indicating that the waste quantity information provided by the industrial contacts is a more reasonable estimate.

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* Because of the presence of iron, aluminum, silicon, and magnesium in the chromite ore, recycling of the total quantity of filter residue to the kiln would lead to the buildup of these undesirable impurities.

The geographical distribution of the chromium wastes from sodium dichromate production was calculated on the basis of the production capacity and locations of the sodium dichromate plants in each U. S. Bureau of Census region (Table 1).

Chromium Wastes from the Textile Industry

Chromium wastes from textile processing result mainly from the chrome mordant dyeing of wool for garments and carpeting. In the past, chromate oxidizers were used for the sulfur dyeing of cotton products, but this practice is expected to be discontinued under environmental pressures.

Estimates of chromium consumption and waste generation in the wool textile industry were obtained through contacts with various textile trade organizations. The American Dye Manufacturers Institute estimated that approximately 25 percent of all wool processed in the United States is chrome dyed, and indicated that about 1 lb of chromium is consumed per hundred lb of wool dyed.[2583] Representatives of the Northern Textile Association (NTI), on the other hand, felt that the portion of wool subjected to chrome mordant dyeing is closer to 35 or 40 percent of the total.[2590] NTI has also indicated that the 40 percent figure is believed to be more accurate and this was used in the calculation of the total waste quantity. Based on the figure that 190 million lb of wool were processed in 1971,[2584] this total has been estimated to be 760,000 lb per year as sodium dichromate.

The chrome mordant dye wastes usually occur in highly diluted forms (1-100 ppm Cr) in combined waste streams from the many other processes used in textile mills, and the chromium present may either be in the trivalent or hexavalent state.

The geographical distribution of these chrome mordant dye wastes was calculated on the basis of the regional distribution of "value added by manufacture" dollar amounts for the wool weaving and finishing industry and by Bureau of Census regions (Table 1). The chromium wastes from the textile mills are found mostly in the Census regions I, II and V, while the remaining regions contribute only an insignificant proportion of the total waste load.

Chromium Waste from Leather Tanning

The basic chromic sulfates are produced in large quantities for use in the leather tanning industry, and are incorporated in various proprietary chrome tan mixtures. These basic chromic sulfate tanning solutions can either be made commercially and supplied to the tanning industry, or be prepared directly in the tanning vats. The normal preparation process is the reduction of a sodium dichromate solution with either an organic material or sulfur dioxide. The organic reduction using crude molasses, corn sugar, and sometimes even sawdust is the older and more widely used method. Sulfur dioxide, when used, performs the dual role of reducing agent and, upon oxidation, of furnishing the required sulfate. If sugar is used, sulfuric acid must be added.

The leather industry creates very large volumes of chromic sulfate wastes in aqueous solutions from the chrome tanning and subsequent washing of the hides. Hide tanning essentially consists of removing organic matter from the hides, and this organic matter, if allowed to build up in the chrome tanning solutions, would interfere with the tanning process. The tanning solutions are therefore normally dumped after being used once or possibly twice.

Approximately 32 million hides (cattle hide equivalent) were tanned in 1960.[0087] Hide tanning volume is believed to have remained constant. About 70 percent of all U.S. leather is used for upper leather on shoes, and virtually all of this is chrome tanned. A study on the treatment of chrome tanning wastes indicates that 1,800 lb of chromium is discharged for every 2,500 hides.[1187] The estimate of 16 million lb of chromium waste is in reasonable agreement with the Booz-Allen figures. In addition, the figures agree, within a factor of two, with the waste generation factor estimated by Stanley Consultants (when a hide weight of 40 lb is assumed).[0513] Very little waste stream segregation is performed in the tanning industry and the 2-12 ppm trivalent chrome concentration in the diverse mixture of brines, fat, acids and large amounts of rinse water constitute a fairly typical waste stream. The geographical distribution of these wastes was calculated on the basis of the regional distribution of "value added by manufacture" dollar amounts for the leather tanning and finishing industry and by Bureau of Census regions (Table 1).

Chromium Wastes from Cooling Tower Blowdown

Chromium compounds are added to cooling water as fungicides, slimicides and anti-corrosion agents. Accurate figures or even general estimates on the amounts of chromium compounds discharged from cooling towers and similar equipment are difficult to obtain for the following reasons:

(1) The large number and diversity of cooling and water circulating equipment;

(2) The wide variation in applications for this type of equipment;

(3) The diversity of proprietary water treatment additives which might contain chromium.

Discussions with the Cooling Tower Institute (CTI) revealed that on the basis of a survey by the Institute, 6.5 million lb of sodium chromate (Na_2CrO_4) were used per year for the operation of 856 cooling towers. CTI had no estimate of the total number of cooling towers in the United States, although it was indicated that half of the requirement for cooling towers lies in the southern United States.[2262]

The total chromium loss from cooling tower blowdown is assumed to be equal to the total sodium dichromate demand for anti-corrosion purposes, at 22 million lb per year. The total quantity of blowdown, i.e., cooling water removed to prevent mineral buildup in cooling systems, is in the multiple millions of gal. per year. Cooling tower blowdown normally contains 10 to 30 ppm of hexavalent chromium.

The geographical distribution of the chromium losses from cooling tower blowdown was calculated on the basis that 50 percent of the total waste load was contributed by the Bureau of Census regions V, VI, and VII, while the remaining 50 percent was distributed according to the population in each Census region (Table 1).

Chromium Wastes from the Photographic Industry

Chromium wastes from the photographic industry are generated in the gravure and leather press plate making operations. The industry purchases only the ammonium chromates and appears to be the only consumer of these low volume chromate salts. Chromate solutions at about 4 to 5 percent are used to sensitize and polymerize gelatin coatings over copper plates when exposed to light coming through a photo negative. Unexposed chromate coated gelatins are then washed away in water streams thereby exposing portions of the plate for etching. Chromates occur as wastes from washing the plates as well as from the chromate tanks which require dumping at 4 to 6 month intervals. An average size tank or tray contains 5 to 10 gal. of the solution. These tanks are normally emptied down a sink without any processing. An estimated 500 such plants are performing this type of operation across the nation, and the total quantity of ammonium dichromate discharged amounts to approximately 4,000 lb per year.[2235,2250]

The geographical distribution of these ammonium dichromate wastes was calculated on the basis of the population distribution in the United States (Table 1).

Wastes of Hexavalent Chromium Salts of Potassium

The potassium chromium compounds can be expected to replace the usual sodium compounds in specific cases where the change in cation improves the process in question. Use of the potassium compounds can occur in nearly every process where the sodium compound is used but it is more expensive and this restricts the usage. The potassium salt consumption and waste amounts represent 3 percent of the sodium salt volume.[2250] The total waste load, calculated as potassium dichromate, amounts to 2.5 million lb per year. The geographical distribution of the potassium chromate/dichromate wastes was assumed to be the same as the geographical distribution of the sum total sodium chromate/dichromate wastes from the metal finishing and textile industries and cooling tower blowdown (Table 1).

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WASTES OF INORGANIC CYANIDES

The principal source of cyanide wastes is the electroplating industry where cyanide compounds are used extensively to make up the plating baths. Waste streams from the electroplating industry contain varying amounts of cyanides ranging from 0.5 to 20 percent, normally in an alkaline solution along with cadmium, copper, zinc, nickel, and chromium compounds. It is estimated that 21 million lb of cyanides are discharged through electroplating wastes each year. The geographical distribution of these electroplating wastes was calculated on the basis of the distribution of "value added by manufacture" dollar amounts for finished metal products in the United States (Table 1). A detailed discussion of the cyanide wastes from the electroplating industry can be found in the report "Wastes from the Electroplating Industry".

The less toxic ferrocyanide is a component of the iron blue and the chrome green pigments. Cyanide wastes are generated in paint manufacture as a result of the kettle washings and equipment cleanup, and are found in the solvent-based waste paint sludges, which typically contain 27.5 percent pigments, 25.0 percent binders, and 47.5 percent organic solvents. Approximately 45,000 lb of cyanides are lost through the 37 million lb of solvent-based waste paint sludges generated each year. The geographical distribution of these waste paint sludges was calculated on the basis of the regional distribution of "value added by manufacture" dollar amounts for paints and allied products in the United States (Table 1). A more complete discussion of the cyanide wastes from paint manufacture and the assumptions used in the computation of the waste quantities can be found in the report "Toxic Paint Wastes".

The paint residues left in used paint containers constitute another source of cyanide waste. It is estimated that 310,000 lb of cyanides are lost through these paint residues each year. The geographical distribution of these paint reside wastes was calculated on the basis of the population distribution in the United States (Table 1). Again, a more complete

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discussion of the paint residue wastes can be found in the report "Toxic Paint Wastes".

Cyanide compounds in Department of Defense storage facilities awaiting disposal include sodium, calcium, copper, potassium and silver cyanides, and potassium ferrocyanide and ferricyanide (Table 1), but amount to less than 2,000 lb total. With the exception of calcium cyanide, which has been used as a rodentcide, all the other surplus cyanide compounds were acquired for plating purposes.

TABLE 1

WASTES OF INORGANIC CYANIDES

Source and Material	Bureau of Census Regions									
	I	II	III	IV	V	VI	VII	VIII	IX	Total
					Annual Waste Production (lb/year)					
Cyanides from electroplating	2.78×10^6	6.07×10^6	6.86×10^6	0.96×10^6	1.04×10^6	0.49×10^6	0.77×10^6	0.15×10^6	2.20×10^6	21.32×10^6
Paint Sludge										
Cyanides	1,100	9,900	13,800	2,900	3,850	2,150	3,350	550	7,300	44,900
Sludge	0.92×10^6	8.12×10^6	11.32×10^6	2.40×10^6	3.16×10^6	1.76×10^6	2.74×10^6	0.44×10^6	5.97×10^6	36.83×10^6
Paint Residue										
Cyanides	0.18×10^5	0.57×10^5	0.62×10^5	0.23×10^5	0.47×10^5	0.20×10^5	0.30×10^5	0.13×10^5	0.41×10^5	3.11×10^5
Old Paint	13×10^6	41×10^6	44×10^6	16×10^6	34×10^6	14×10^6	21×10^6	9×10^6	29×10^6	221×10^6
					Stored Wastes (lb)					
Sodium Cyanide	-	1,400	-	-	-	-	-	16	-	1,416
Calcium Cyanide	-	-	-	-	-	-	180	-	25	205
Copper Cyanide	-	100	-	-	-	-	-	32	-	132
Potassium Cyanide	-	-	-	-	2	-	-	-	-	2
Silver Cyanide	-	-	-	-	-	-	-	16	10	26
Potassium Ferricyanide	-	-	-	-	4	-	-	-	-	4
Potassium Ferrocyanide	-	-	-	-	-	12	-	-	-	12

WASTES OF HYDROFLUORIC AND FLUOBORIC ACIDS

Hydrofluoric and fluoboric acids are the two fluorine containing hazardous chemicals more commonly found in industrial waste streams that require specialized handling and disposal. The principal sources of hydrofluoric acid waste* are the spent pickling solutions and the rinse water from the stainless steel pickling process, whereas the principal source of fluoboric acid waste is the rinse water from metal plating. Hydrofluoric and fluoboric acid wastes from these sources are discussed in the following sections of this report.

Hydrofluoric Acid Waste from Stainless Steel Pickling

Steel pickling is the process of chemically removing the oxides and scales formed on the surface of the steel products in the rolling operations. It is usually done between the hot working and cold working phases of the operation. Solutions of inorganic acids are normally used as the pickling solutions. Generally, sulfuric acid or hydrochloric acid is used to pickle carbon steel and solutions of two or three acids, including hydrofluoric acid, are used to pickle stainless steel.

The wastes from the stainless steel pickling come from two sources: (1) the spent pickling solutions containing the concentrated acids and iron salts; and (2) the rinse water from the pickling operation containing dilute acids and iron salts. A typical spent pickling solution may contain 7 percent hydrofluoric acid, 10 percent sulfuric acid, 4 percent iron salts, and traces of other metals such as chromium, nickel, cobalt, etc.†

Information provided by industrial sources indicated that for a manufacturing facility producing 20 tons of stainless steel per day, 200 to

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*Other than the extremely dilute hydrofluoric acid discharges from the fertilizer industry.

†Rollins Environmental Services data.

300 gal. of pickling waste containing 1.5 percent hydrofluoric acid are generated.[2624] On this basis, the waste effluent is estimated to be 140 lb per ton of stainless steel pickled and the hydrofluoric acid loss is approximately 2 lb per ton of stainless steel product. For a total U.S. stainless steel production of 1.4 million tons per year,[2625] the total pickling wastes amount to 196 million lb per year, with a corresponding hydrofluoric acid loss of 2.8 million lb per year. The geographical distribution of these pickling wastes was determined on the basis of the production capacities and locations of stainless steel producing facilities (Table 1).

Fluoboric Acid Waste from Metal Plating

In metal plating, fluoborate baths are sometimes used, particularly for the plating of lead, tin, and their alloys. The main source of waste comes from the liquid entrainment dragged out by the plating products which are subsequently rinsed with water. The aqueous waste effluent thus generated may contain 1 to 2 percent fluoboric acid, 5 percent hydrochloric acid, 2 percent carbon black.* Information provided by industrial sources indicated that the total U.S. consumption of fluoborate baths is an estimated 10,000 gal. per year.[2626] Since the fluoborate baths contain, on the average, 21 to 22 oz of fluoborate per gal., the total net fluoborate waste is about 13,800 lb per year. As the waste effluent contains an average of 1.5 percent of fluoboric acid,† the total fluorine waste effluent amounts to 460 tons per year. The geographical distribution of these wastes was determined on the basis of the distribution of "value added by manufacture" dollar amounts for finished metal products and according to Bureau of Census regions (Table 1).

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*,†Rollins Environmental Services data.

TABLE 1
WASTES OF HYDROFLUORIC AND FLUOBORIC ACIDS

Source and Material	Bureau of Census Regions									
	I	II	III	IV	V	VI	VII	VIII	IX	Total
	Annual Waste Production (lb/year)									
Stainless steel pickling, hydrofluoric acid loss	-	1.96×10^6	0.84×10^6	-	-	-	-	-	-	2.8×10^6
Metal plating and finishing fluoboric acid loss	1.8×10^3	3.9×10^3	4.5×10^3	0.6×10^3	0.7×10^3	0.3×10^3	0.5×10^3	0.1×10^3	1.4×10^3	13.8×10^3

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WASTES OF SPECIFIC ORGANIC CHEMICALS

The determination of the waste forms and quantities of five hazardous organic chemicals has been included in this study. These five hazardous organic chemicals are: acrolein, chloropicrin, dimethyl sulfate, pentachlorophenol, and polychlorinated biphenyls (PCBs). The basis for selecting these particular five organic chemicals are their degree of toxicity, the probability of their presence in significant quantities as solid, semisolid, or concentrated liquid wastes, and the complexity of the treatment that is required in their disposal/recovery.

Of the five hazardous organic chemicals investigated, the polychlorinated biphenyls are the only compound(s) actually found in sizable volumes as wastes. The PCB wastes as well as the wastes of the other four organic chemicals are discussed in individual sections of this report.

Acrolein Wastes

Acrolein is a volatile and highly toxic liquid that is produced in the United States by essentially two manufacturers located in the New Orleans area.[2629,2630] It is prepared almost entirely as an intermediate product or as a starting material for captive in-house applications and only very small quantities of the chemical are being sold commercially. In the production of acrylic acid by vapor phase, for example, the catalytic oxidation of propylene is a two-step reaction with acrolein as the intermediate product.

Since acrolein is flammable, highly irritating, and toxic, extreme care is exercised in its production process to minimize losses to the atmosphere or through the plant waste streams.[2629,2630] The exact quantity of acrolein wastes generated at the two manufacturing plants has not been disclosed, but is believed to be of very low volume and further investigations are not merited.

Chloropicrin Wastes

Chloropicrin is a slightly oily liquid prepared from nitromethane. The product is recovered from the reaction mixture by distillation. The waste effluent from the production process is a clear aqueous solution, typically containing less than 0.01 percent of chloropicrin with 3 percent sodium hydroxide and 20 percent sodium chloride.[2631] One major producer of chloropicrin, Sobin Chemical, mixes the waste effluent with brine solution and sends it to their chlorine plant (in same location) as a feed, forming a closed loop with no direct waste discharge from the chloropicrin manufacturing plant.[2627]

There are currently four major chloropicrin manufacturers in the United States[2627,2628,2631]: Sobin Chemical, Niklor Chemical Company, Dow Chemical Company, and International Minerals and Chemicals Corporation (IMC). Information provided by Niklor Chemical indicated that a total of approximately 600,000 gal. of waste containing less than 0.01 percent chloropicrin is discharged into the Los Angeles County sewage disposal system per year.[2631] Based on a production capacity of 600 tons per year and a 0.01 percent chloropicrin concentration in the aqueous waste stream, the chloropicrin loss at Niklor Chemical was estimated to be 0.04 percent of the chloropicrin production. Assuming the same waste generation factor for the Dow and IMC plants, and negligible chloropicrin loss at the Sobin plant, the total chloropicrin loss in the United States through plant waste water amounts to only 1,700 lb per year. These chloropicrin wastes were distributed geographically according to the locations and production capacities of the chloropicrin plants in each Bureau of Census region (Table 1).

Dimethyl Sulfate Wastes

Dimethyl sulfate is produced almost exclusively by Du Pont. It is prepared in a liquid phase reaction between oleum and dimethyl ether, and the product is separated from the reaction liquid by distillation as the overhead product. The bottom product is recycled back to the reactor and eventually, a viscous, dark brown liquid residue is formed in the bottom of the distillation column. This liquid residue is the major source of dimethyl sulfate waste.[2623] The composition of this waste stream is not known, but is believed to contain much less than 1 percent dimethyl sulfate.[2623] Du Pont has two plants producing dimethyl sulfate, one in West Virginia and one in New Jersey. Each plant generates approximately 4,000 gal. of the liquid residue waste per year.[2623] On this basis, the total waste stream was calculated to be about 120,000 lb per year. As this liquid waste contains much less than 1 percent dimethyl sulfate, the assumption of 0.1 percent dimethyl sulfate concentration indicates that the total dimethyl sulfate loss is about 120 lb per year. These dimethyl sulfate wastes were assumed to be equally distributed in the states of West Virginia and New Jersey (Table 1).

Pentachlorophenol Wastes

Pentachlorophenol is supplied by essentially four major producers.[2621] The loss of pentachlorophenol through plant waste streams during the manufacturing process is very small. According to one major producer, only 100 lb per year of pentachlorophenol are lost in the waste water for an annual pentachlorophenol production of 4 to 5 million lb.[2620] The total U. S. production of pentachlorophenol is about 20 million lb per year. Based on a waste generation factor of 20 lb pentachlorophenol loss per million pound product, the total pentachlorophenol loss in the United States amounts to only 400 lb per year. These pentachlorophenol wastes were distributed geographically according to the locations and production capacities of pentachlorophenol plants in each Bureau of Census region (Table 1).

A major application of pentachlorophenol is for termite and mold controls on lumber products in wood and construction industries. For wood preserving, the products are treated with 5 to 10 percent solution of pentachlorophenol in organic solvent under pressure. Pentachlorophenol is absorbed into the wood products. After the wood treating process, the products are subject to vacuum to remove any remaining, unabsorbed liquid entrainment. The whole wood treating operation is carried out in a

TABLE 1
WASTES OF HAZARDOUS ORGANIC CHEMICALS

Source and Material	Bureau of Census Regions									
	I	II	III	IV	V	VI	VII	VIII	IX	Total
	Annual Waste Production (lb/year)									
Acrolein wastes	-	-	-	-	-	-	-	-	-	-
Chloropicrin production wastes, as chloropicrin	-	-	1,100	-	-	-	-	-	600	1,700
Dimethyl sulfate production wastes, as dimethyl sulfate	-	60	-	-	60	-	-	-	-	120
Pentachlorophenol production wastes, as pentachlorophenol	-	-	200	100	-	-	-	-	100	400
PCB wastes, as PCB	0.98×10^6	3.10×10^6	3.35×10^6	1.25×10^6	2.55×10^6	1.06×10^6	1.61×10^6	0.69×10^6	2.21×10^6	16.80×10^6

closed system, so that there is practically no pentachlorophenol loss in the process.[2622]

Wastes of Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are a family of organic chemicals varying in physical state from mobile oily liquids to fine white crystals and hard transparent resins.* PCBs were first identified as potential food contaminants in 1966 and since that time have been found throughout the global environment. Because of the similarity of PCBs to the chlorinated hydrocarbon pesticides such as DDT in terms of toxicity effects, persistence and wide dispersal in the environment, and tendency to accumulate in food chains, the release of PCBs into the environment has caused growing concern in recent years.

In the United States, PCBs have been manufactured by a single producer, the Monsanto Company, and marketed under the trade name "Aroclor". Because of the findings of the impact of PCBs on the environment, Monsanto has restricted sales of Aroclors based on consideration of either the possibility of contamination of food products or its inability to control or monitor possible PCB losses. In November 1971, Monsanto released figures for U. S. domestic sales of Aroclors during the period 1963 to 1970 according to category of use and grade of Aroclor (Table 2).[2615] These figures indicate that prior to Monsanto's voluntary reduction of sales in September 1970, approximately 60 percent of the sales were for closed-system electrical and heat transfer uses, 25 percent for plasticizer applications, 10 percent for hydraulic fluids and lubricants, and less than 5 percent for miscellaneous applications such as surface coatings, adhesives, printing inks, and pesticide extenders. The fraction of sales for use in confined systems, primarily as dielectric fluids for transformers and

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*There are about 210 possible PCB compounds, about 50 of which are produced commercially and usually exist as mixtures. The commercial mixtures are sold under the trade name Aroclor and are distinguished by numbers--the first two digits 12 specify polychlorinated biphenyls and the last two digits the approximate percentage of chlorine in the mixture. The more highly chlorinated PCBs are more persistant, whereas the less chlorinated ones are more toxic.

TABLE 2

PCB MANUFACTURING AND SALES DATA FROM MONSANTO INDUSTRIAL CHEMICALS CO.

1957 THROUGH 1971
(Thousands of Pounds)

	1957	1958	1959	1960	1961	1962
U.S. production*				37,919	36,515	38,353
Domestic sales	32,299	26,061	31,310	35,214	37,538	38,043
Domestic sales by category						
Heat transfer	-	-	-	-	-	157
Hydraulics/lubricants	1,612	1,549	2,685	2,523	4,110	3,915
Misc. industrial	704	755	1,569	1,559	2,114	1,681
Transformer	12,955	5,719	5,984	7,921	6,281	7,984
Capacitor	17,028	14,099	16,499	16,967	15,935	15,382
Plasticizer applications†	-	3,939	4,573	6,244	9,098	8,924
Petroleum additives	-	-	-	-	-	-
Domestic sales by PCB grade						
Aroclor 1221	23	16	254	103	94	140
Aroclor 1232	196	113	240	155	241	224
Aroclor 1242	18,222	10,444	13,598	18,196	19,827	20,654
Aroclor 1248	1,779	2,559	3,384	2,827	4,023	3,463
Aroclor 1254	4,461	6,691	6,754	6,088	6,294	6,325
Aroclor 1260	7,587	5,982	6,619	7,330	6,540	6,595
Aroclor 1262	31	184	359	326	361	432
Aroclor 1268	-	72	102	189	158	210

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*Production amounts prior to 1960 are not available.

†Amounts for plasticizer applications prior to 1958 are not available.

TABLE 2 - CONTINUED

PCB MANUFACTURING AND SALES DATA FROM MONSANTO INDUSTRIAL CHEMICALS CO.
1957 THROUGH 1971
(Thousands of Pounds)

	1963	1964	1965	1966	1967	1968	1969	1970	1971	1972
U.S. production	44,734	50,833	60,480	65,849	75,309	82,854	76,387	85,054	40,471	25-30,000
Domestic sales	38,132	44,869	51,796	59,078	62,466	65,116	67,194	73,061	37,635	25-30,000
U.S. export sales	3,647	4,096	4,234	6,852	8,124	11,231	10,624	13,651	9,876	?
Domestic sales by category										
Heat transfer	582	929	1,237	1,766	2,262	2,529	3,050	3,958	3,480	-
Hydraulics/lubricants	3,945	4,374	4,616	4,258	4,643	5,765	8,039	7,403	1,643	-
Misc. industrial	1,528	1,692	1,841	1,779	1,426	1,283	1,079	1,627	578	-
Transformer	7,290	7,997	8,657	8,910	11,071	11,585	12,105	13,828	11,528	25-30,000
Capacitor	15,606	19,540	23,749	28,884	29,703	29,550	25,022	26,708	17,305	25-30,000
Plasticizer applications	9,181	10,337	11,696	13,481	13,361	14,404	16,460	19,537	3,102	-
Petroleum additives	-	-	-	-	-	-	1,439	-	-	-
Domestic sales by PCB grade										
Aroclor 1221	361	596	369	528	442	136	507	1,476	1,600	300
Aroclor 1232	13	13	7	16	25	90	273	260	211	300
Aroclor 1242	18,510	23,571	31,533	39,557	43,055	44,853	45,401	48,588	21,000	4,000
Aroclor 1248	5,013	5,238	5,565	5,015	4,704	4,894	5,650	4,073	261	-
Aroclor 1254	5,911	6,280	7,737	7,035	6,696	8,891	9,822	12,421	5,800	6,000
Aroclor 1260	7,626	8,535	5,831	5,875	6,417	5,252	4,439	4,890	1,750	600
Aroclor 1262	414	446	558	768	840	720	712	1,023	-	-
Aroclor 1268	284	190	196	284	287	280	300	330	-	-

capacitors, has increased to approximately 90 percent in 1971 and 100 percent in 1972. To meet the problem of scrap disposal, Monsanto has set up a disposal system with a capacity of 10 million lb per year for their customers. Within a year of announcement of the service, 500,000 lb of waste PCBs had accumulated at the disposal site, where it is held in storage, pending the completion of the incinerator.[2638]

Solid, semi-solid, and concentrated liquid PCB wastes are generated as equipment or products containing these materials are replaced and discarded. Although the current application of PCBs has been limited principally to electric equipment and utilities, PCB wastes continue to be generated from applications which were previously acceptable. Information on the forms and composition of some typical PCB waste streams was provided by Rollins Environmental Services and is summarized in this report (Table 3).

Estimates on the PCB losses by disposal into incinerators, dumps, and landfills were made on the basis of the useful service life of PCBs in transformers, capacitors, plasticizers, and heat exchangers. The general assumptions employed were those as suggested by Nisbet and Sarofim[2638]:

(1) only 10 percent of the PCB sales for transformer fluid is to replace oil that is scraped and the remaining 90 percent is for new units as transformers are fairly permanent installations;

(2) a useful life of approximately 10 years for capacitors and heat exchangers, thus the rate of disposal of PCBs from these applications is equal to the corresponding sales volume 10 years ago;

(3) a useful life of one year for plastic objects and a rate of disposal of plasticizers into dumps equal to 90 percent of the sales, the residual 10 percent is accounted for by the rate of vaporization of plasticizers.

Calculations based on the assumptions stated above indicate that 8,400 tons of PCBs ended up in incinerators, dumps and landfills in 1972. These PCB wastes were distributed geographically according to the population

TABLE 3

EXAMPLES OF PCB WASTES

Waste Description	Physical Form	Waste Source
90 percent polychlorinated biphenyls; 10 percent alpha methyl styrene.	Liquid	Chemical
Spent dielectric fluid of the arochlor-inerteen type; essentially 100 percent polychlorinated biphenyls and their breakdown products.	Liquid	Utilities, power equipment manufacture; utilities service
Heat transfer oil containing 20 percent polychlorinated biphenyls, 80 percent lube oil.	Liquid	Chemical
Spent dielectric fluid of the askarel-pyranol type containing 50 percent or more polychlorinated biphenyls, 30-40 percent chlorinated diphenyl ether; breakdown products and water.	Liquid	Utilities service
10 to 90 percent polychlorinated biphenyls (PCB) with diphenyl and diphenyl oxide (heat exchanger displacement).	Liquid	Rubber
5 to 99 percent PCB (containing chlorine in the range of 20 to 60%) mixed with solvents, oils, water and dirt (electrical capacitors).	Liquid	Utilities; power equipment
2 to 10 percent PCB by weight in capacitors including shell and impregnated membranes.	Liquid and Solid	Utilities; power equipment
Rags and filter aid contaminated with various compounds of PCB (spills and filtering).	Solid	Utilities; power equipment

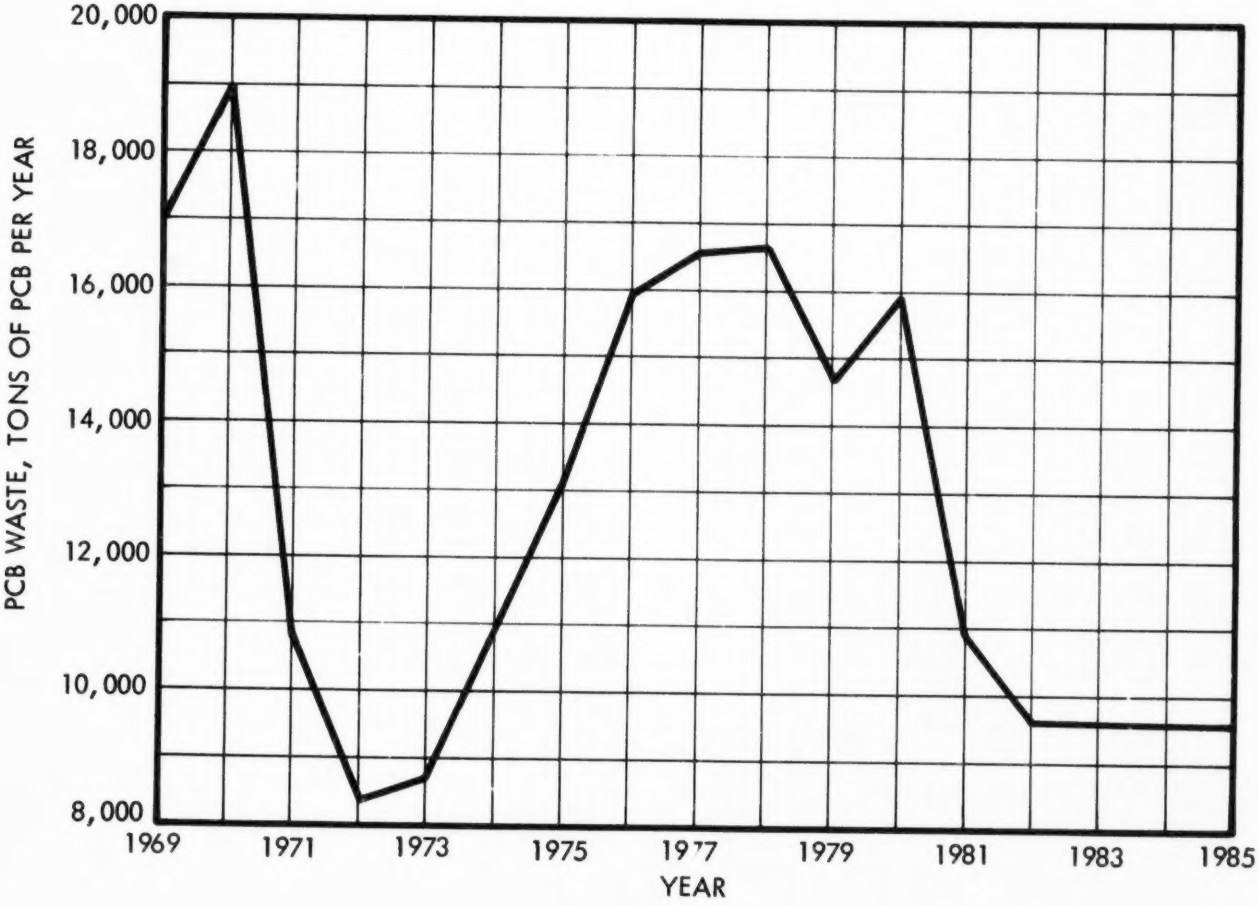

Figure 1. PCB wastes requiring disposal per year.

distribution in the United States (Table 1). The same set of assumptions was also used to estimate the total quantity of PCB wastes requiring disposal per year for the period 1969 to 1982 (summarized here in Figure 1). The results of the computations indicate that after Monsanto restricted its PCB sales and PCB application as plasticizers was discontinued, the PCB wastes generated per year dropped sharply from 19,000 tons in 1970 to 10,800 tons in 1971. However, because of the large increases in PCB sales as dielectric fluid for capacitors during 1963 to 1970, the PCB wastes generated per year will increase again to a high of 16,600 tons in 1977 and 1978, remain relatively unchanged till 1980, and thereafter decrease to approximately 10,000 tons from 1982 on.

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EXPLOSIVE, PROPELLANT AND CHEMICAL WARFARE MATERIEL

Obsolete conventional and chemical ammunition, and explosive wastes constitute a high volume, high hazard disposal problem. A large portion of these wastes must be treated by special techniques at National Disposal Sites under civilian or military cognizance, to minimize or eliminate danger to the public and impact upon the environment.

Almost all explosive, propellant, and chemical warfare materiel wastes may be divided into two major categories, based on origin:

(1) Obsolete and surplus ammunition and ordnance materiel scheduled for disposal by the Armed Services;

(2) Wastes generated in the manufacture of explosives, military and commercial explosive devices, and other ordnance items.

The hazardous materials contained in explosive, propellant and chemical warfare materiel wastes have been subdivided for convenience, because of the large number involved, into seven classes. The seven classes, and typical hazardous materials representative of the classes, are:

(1) Initiating Agents and Primers--Mercury Fulminate, Lead Azide, Lead Styphnate, DDNP, Tetrazene, Copper Acetylide, DPEHN.

(2) Propellants, Nitrocellulose Based--Smokeless gunpowder, nitrocellulose, Gelatinized nitrocellulose, rocket propellant (double-base), ballistite, pyrocellulose, composition D-2, nitroglycerin.

(3) Propellants, Composite/Other--Rocket propellant TP-H-1011, Rocket propellant TP-H-1016, Rocket Propellant ANB-3066, Ammonium Perchlorate, Chlorine Trifluoride, IRFNA, Perchloryl Fluoride.

(4) High Explosives--Ammonium Picrate, Glycol Dinitrate, Picric Acid, PETN, TNT, Dynamite, Composition A, Composition B, Composition B2, Composition C, RDX, HMX, Tetryl, Pentolite, Cavity Hot Melt, Plastic Explosive.

(5) Pyrotechnics and Incendiaries--White Phosphorus, Red Phosphorus, Napalm, NP (Thickened Gasoline, with Napalm), PTI (Incendiary Mixture), Magnesium Powder, Thermite, SGF2 (Fog, Oil, Smoke Mixture).

(6) Riot Control Agents--Chloracetophenone Tear Gas (CN), Tear Gas Irritant (CS), BBC (Brombenzylcyanide), CN-DM (Burning Mixture of CN and DM), CNS (Chloracetophenone and Chlorpicrin), DA (Diphenyl chloroarsine), DM (Adamsite, diphenylaminochloroarsine).

(7) Chemical Warfare Agents--GB, VX, Lewisite, Sulfur Mustard (H, HD), Nitrogen Mustards.

Obsolete Munitions

Obsolete and surplus conventional ammunition and ordnance material scheduled for disposal by the Armed Services have been inventoried for each Department of Defense facility in the United States as of July 28, 1972 by the Joint AMC/NMC/AFLC/AFSC Commanders Panel on Disposal Ashore of Ammunition.[2586] The inventory indicates the number of rounds and gross weight of each Federal Stock Catalog item of ammunition or ordnance material at each facility. There are 39 such facilities, located in 24 states (Table 1). With the assistance of Navy-furnished information on the hazardous materials contained in the individual ammunition items,[2594,2669] a state-by-state inventory of the quantities of each of the hazardous material classes used as fill and the associated quantities of obsolete ammunition was compiled by TRW (Table 2). The inventory represents the quantities in hazardous obsolete conventional ordnance device stockpiles scheduled for disposal as of July 28, 1972 for the U.S. Army, and conventional obsolete ordnance device stockpiles scheduled for disposal by the U.S. Navy as of November 30, 1972. The inventory does not include data on the quantities and locations of obsolete and surplus lethal chemical agents or ordnance devices containing lethal chemical agents. Such information is not available, to the level of detail presented here (Table 2).

The obsolete conventional ordnance devices scheduled for disposal encompass virtually the entire range of conventional munitions--from minute fuze components, weighing fractions of an ounce, to 280 mm artillery projectiles over 600 lb in weight. The number of individual rounds and components of obsolete munition are in the tens of millions. The numbers of types of

TABLE 1

DEPARTMENT OF DEFENSE FACILITY STORAGE POINTS FOR OBSOLETE CONVENTIONAL AMMUNITION

State	Facility
Alabama	Anneston (A)
Arizona	Navajo (A)
California	Sierra (A), Alameda (N), North Island (N), El Toro (N), Miramar (N), Moffett Field (N), Concord (N), Seal Beach (N)
Colorado	Pueblo (A)
Florida	Jacksonville (N), Key West (N), Cecil Field (N)
Georgia	Brunswick (N)
Hawaii	Oahu (N)
Illinois	Savanna (A)
Indiana	Crane (N)
Kentucky	Lexington (A)
Maryland	Indian Head (N)
Nevada	Hawthorne (N)
New Jersey	Earle (N)
New Mexico	Fort Wingate (A)
New York	Seneca (A)
North Carolina	Cherry Point (N)
Oklahoma	McAlester (N)
Oregon	Umatilla (A)
Pennsylvania	Letterkenny (A)
Rhode Island	Quonset Point (N)
South Carolina	Charlestown (N), Beaufort (N)
Texas	Red River (A), Corpus Christi (N)
Utah	Tooele (A)
Virginia	Norfolk (N), Virginia Beach (N), Yorktown (N), Oceana (N), St. Juliens Creek Annex (N)
Washington	Bangor (N), Keyport Bangor Annex (N)

(A) = Army
(N) = Navy or Marine

TABLE 2

OBSOLETE CONVENTIONAL MUNITIONS

HAZARDOUS MATERIAL CONTENTS AND GROSS WEIGHT DISTRIBUTION BY STATE - SCHEDULED FOR DISPOSAL BY THE DEPARTMENT OF DEFENSE[+] 2586,2594,2668,2669

	Weight of Explosive, Incendiary, Pyrotechnic and Riot Control Agent Fill, in lb							Weight of Obsolete Munitions Containing Each Fill Category, in lb						
	(1)	(2)	(3)	(4)	(5)	(6)	TOTAL	(1)	(2)	(3)	(4)	(5)	(6)	TOTAL*
Alabama	900	539,664		1,118,677	6,802	15,666	1,681,709	3,446,600	3,727,600		3,095,600	564,600	32,400	6,812,800
California	23,608	1,327,982	159	621,303	128,819	2,595	2,104,466	9,423,300	10,948,700	1,200	9,882,600	358,300	12,100	13,002,000
Colorado	2,210	962,052		317,692		81	1,282,035	8,403,000	8,403,000		9,073,800		200	9,073,800
Florida	1	812		397	38		1,248	1,400	6,700		2,600	111		19,300
Georgia					11		11					26		26
Hawaii	4,151	265,317	49	1,879,438	63,179	104	2,212,238	157,000	1,535,800	4,700	3,172,000	195,200	1,500	4,954,200
Illinois	47,856	1,059,183		752,641			1,859,410	19,157,800	19,114,200		19,192,600			20,288,600
Indiana	16,790	6,086,532	15	6,678,784	416,618	186	13,198,925	7,916,100	22,694,000	30,000	20,581,392	7,340,700	320	36,722,200
Kentucky	1,921	855,000		302,314		37,971	1,197,206	6,243,200	6,243,200		6,385,000		82,800	6,554,000
Maryland	17	15,617		20,304			35,938	35	25,200		37,600	81		63,300
Nevada	93,670	3,964,246	117	12,824,056	774,514	7,610	17,664,213	4,060,300	15,330,300	7,600	25,049,800	2,443,000	63,000	48,369,400
New Jersey	6,454	207,706	49	524,258		440	738,907	699,400	957,800	900	1,612,200	660,500	1,200	2,686,700
New York	6,786	1,238,392		735,751			1,980,929	2,490,000	6,588,600		3,247,200			7,363,800
North Carolina	5,000			2,808	21		7,829	12,500			5,200	31		19,100
Oklahoma	35,654	13,997,459	394	6,479,680	911,987	952	21,426,126	35,121,200	54,440,200	786,000	46,565,400	34,482,800	1,300	69,542,500
Oregon	4,396	1,937,082		1,353,290		946,944	4,241,712	16,642,400	16,642,400		17,107,000		2,486,000	19,128,400
Pennsylvania	11,398	3,459,496		2,485,059			5,955,353	28,515,800	24,423,000		29,202,000			30,267,000
Rhode Island					34		34					79		81
South Carolina	1,143	177,665		314,027	94,331	113	587,279	79,700	713,100	232	864,400	217,700	226	1,752,100
Texas	7,936	407,675		113,149	433		529,193	3,632,200	3,674,200		3,468,200	130,135		3,674,300
Utah	1,099	478,18[illegible]		129,238			608,518	4,037,400	4,037,400		4,037,400			4,037,400
Virginia	32,002	399,348	176	658,333	178,545	4,795	1,273,199	395,600	1,701,800	2,600	1,967,500	349,200	9,200	4,782,500
Washington	2,022	447,479	7	1,463,890	7,915	176	1,921,489	52,300	2,797,000	800	2,874,100	40,200	360	6,310,700
Continental United States	305,014	37,821,828	966	38,775,092	2,942,303	1,017,633	80,862,836	150,487,300	204,004,200	834,000	207,405,500	46,783,200	2,690,600	301,237,344

Code: (1) Initiating Agents and Primers; (2) Propellants, nitrocellulose based; (3) Propellants composite/other; (4) High explosives; (5) Pyrotechnics and Incendiaries; (6) Riot Control Agents

*Will not agree with sum of weights of obsolete munitions containing the individual fill categories because of redundancies due to multiple fills in many ordnance items.

+U. S. Army - as of July 28, 1972; U. S. Navy - as of November 30, 1972 individual rounds and components stored for disposal are in the tens of thousands--over 1,100 Federal Stock Numbers in California alone. There are approximately 301,000,000 lb of obsolete conventional ammunition, containing almost 81,000,000 lb of explosive or otherwise hazardous materials. The detailed information presented on the quantities and locations of these hazardous wastes was developed by the Joint Logistics Commanders Panel, to scope the problem as first step in accomplishing the objective of developing "a joint plan for disposal ashore of ammunition by ecologically acceptable means, due to the restrictions on deep water dumping."[2586]

Prior reports have indicated a portion of the surplus chemical munitions stored at U. S. Army facilities (3,071 tons of Mustard; 2,085 tons of GB; and 2,700 tons of Phosgene).[1623] The organophosphorus chemical warfare agents (GB and VX, the "nerve gases") are contained in artillery shells, rocket warheads, bombs, mines and sprayers (see Table 1, page 239, Volume VII of this report). Mustard is contained in a similar array of stored munitions (Table 3). The major materials resulting from the destruction of the lethal chemical warfare agents scheduled for disposal over the next 10 years amount to some 70,000 tons of calcium and sodium chloride, sulfate, sulfite, fluoride, carbonate and phosphate, and sodium methylisopropylphosphonate, at nine locations (Table 4).[1732]

The explosive-contaminated inert wastes generated by ordnance device manufacture are almost always contaminated packaging materials--paper, plaster, cardboard fiberboard and wood.

Hazardous wastes generated in the manufacture of explosives, military and commercial explosive devices, and other ordnance devices are in excess of 48,000,000 lb, annually (Table 5). Of this total, close to 23,000,000 lb are explosive scrap. The data for explosive contaminated inert wastes is incomplete, and the estimate for such hazardous wastes (25,506,000 lb) represents only a portion of the total. Data for hazardous wastes produced by Government Owned, Contractor Operated (GOCO) plants under U. S. Army cognizance was obtained directly from the Army.[2637] Data on the explosive waste output of the contractor operated plants under Atomic Energy Commission direction, was furnished by Mason and Hanger Silas Mason Co. Inc.,[2632]

TABLE 3

SOME U. S. MUNITIONS CONTAINING MUSTARD[958]

Ammunition	CW Agent	Delivery Device	Ammunition Wt/lbs	CW Agent Wt/lbs	Explosive Wt/lbs	Propellant Wt/lbs
Shells						
M60 Cartridge	HD	105mm howitzer	43	3.0	0.3	2.75
M2/M2A1 Cartridge	HD	4.2 in mortar	25	6.0	0.7	0.4
M2/M2A1 Cartridge	HT	4.2 in mortar	25	5.8	0.7	0.4
M110 Projectile	HD	155mm howitzer	99	9.7	0.8	None
M104 Projectile	HD	155mm howitzer	95	11.7	0.8	None

TABLE 4

ESTIMATED SALT TONNAGES FROM DISPOSAL OF LETHAL CHEMICAL WARFARE AGENTS[1732]

Site		Estimated Salt Tonnage*
Edgewood Arsenal, Maryland		3,400
Pine Bluff Arsenal, Arkansas		7,800
Rocky Mountain Arsenal, Colorado		13,000†
Tooele Army Depot, Utah		25,000
Umatilla Army Depot, Oregon		7,300
Anneston Army Depot, Louisiana		5,700
Pueblo Army Depot, Colorado		3,900
Newport Army Ammunition Plant, Indiana		3,000
Lexington Blue-Grass Army Depot, Kentucky		900
	Total	70,000

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*Mixtures of calcium chloride, sulfate, sulfite, fluoride, carbonate and phosphate.

†4,350 tons from disposal of GB; 7,900 tons from disposal of mustard,[0958] comprised of mixtures of sodium chloride, sulfate, sulfite, fluoride, carbonate, phosphate, and methylisopropylphosphonate.

TABLE 5.
EXPLOSIVE MANUFACTURING WASTES
POUNDS PER YEAR SOLID WASTES* DISCHARGED--BY STATE[2448,2496,2596,2632, 2637, 1287,2297,1623]

State	Initiating Agents & Primers		Propellants, nitro-cellulose based		Propellants Composite/Other		High Explosives		Pyrotechnics & Incendiaries		Total		
	Scrap Explosives	Contam. Inert	Scrap Explosives	Contam. Inert	Scrap Explosives	Contam. Inert	Scrap Explosives	Contam. Inert	Scrap Explosives	Contam. Inert	Scrap Explosives	Contam. Inert	All haz. Wastes
Alabama	1,800	700					22,000	73,000			24,000	74,000	98,000
Arzona							3,700				3,700	-	3,700
Arkansas									548,000	639,000	548,000	639,000	1,187,000
California	4,100	1,400			1,043,000	218,000	2,900		6,800		1,057,000	219,000	1,276,000
Colorado	10	1,800					3,700				3,700	1,800	5,500
Connecticut									11,000		11,000		11,000
Illinois			132,000				3,898,000	1,095,000			4,030,000	1,095,000	5,125,000
Indiana	132,000		3,700				133,000				269,000		269,000
Iowa							1,819,000	862,000			1,819,000	862,000	2,681,000
Kansas	138,000	3,614,000	1,877,000	3,979,000			138,000	3,614,000			11,207,000	2,153,000	13,360,000
Louisiana			37,000				1,643,000				1,680,000		1,680,000
Massachusetts							22,000				22,000		22,000
Minnesota			21,900								21,900		21,900
Missouri			219,000				222,000	72,300	1,200		442,000	72,000	513,000
Nebraska			219,000	60,200			219,000	60,200			438,000	120,000	558,000
New Jersey	1,100	237,000	365,000	365,000			7,300				373,000	592,000	975,000
New Mexico	25,800	10,300					126,000	50,000			152,000	60,000	212,000
New York	200	400					20,500		1,500		22,000	400	23,000
Ohio	600	200					11,800	300			12,400	500	13,000
Pennsylvania	500	152,000					51,300	577,000			52,000	729,000	781,000
Tennessee	10						1,419,000	243.000			1,419,000	243,000	1,662,000
Texas							110,000	44,000	14,600	-	125,000	44,000	169,000
Utah			148,000	76,000	713,000	115,000	3,700	91,300	200,000		1,065,000	282,000	1,347,000
Virginia	10		2,871,000	4,344,000			3,012,000	4,636,000			5,883,000	8,980,000	14,863,000
Washington							192,000	274,000			192,000	274,000	466,000
West Virginia			11,000								11,000		11,000
Wisconsin			141,000				730,000						871,000
Total	304,000	4,018,000	6,046,000	8,824,000	1,756,000	333,000	13,810,000	11,692,000	783,000	639,000	22,699,000	25,506,000	48,205,000

*Excluding explosive wastes discharged as solute or suspensoid in facility outfalls.

indicated a current annual scrap explosive generation rate of 598,000 lb per year, and an estimate of 230,000 lb per year of contaminated inert. Direct information from several of the Air Force contractors was used in projecting an annual hazardous waste output of 2,313,000 lb (1,904,000 lb of scrap propellant and 409,000 lb of contaminated inert waste).[2596,2496,2448] Other than partial data presented in an earlier report,[1623] there was no data directly available from non-military explosives and commercial explosive device manufacturers. An estimate was made, accordingly, of scrap explosives generated by this segment of the industry, using Bureau of the Census employee population figures, Bureau of Mines explosives production data for 1971, in-house knowledge of type of explosive produced at various locations, and "Waste Factors" of 0.3 percent for all explosives other than initiating agents. For initiating agents, a waste factor of 0.1 percent was used.

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2669. U. S. Navy ships parts control center. Magnetic tape S.N. 78664. Ownership code 2 assets.

RADIOACTIVE WASTES

The radioactive wastes created and stored by the AEC were documented in the preceding study performed by Booz-Allen Applied Research. The wastes stored by commercial firms in Agreement State sites were not included in the data provided by the AEC. Early in 1973 the Kentucky State Department of Public Health with the support of the Office of Radiation Programs, the Office of Research and Monitoring and the Office of Solid Waste Management Programs of EPA undertook a program to transcribe their records of the radioactive wastes stored at the Maxey Flats site onto computer compatible media. These data are particularly important since the Maxey Flats site is estimated to receive forty-five percent of all non-AEC stored wastes. However, these data have not been reviewed or analyzed to any significant degree at the present time (August 1973). Therefore, no quantitative data are presented.